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Carbonation of Cement-Solidified Hazardous Waste

by

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ABSTRACT

Solidification technology can be an effective process for treating a variety of difficult to manage waste materials containing heavy metals prior to reuse or disposal. There are numerous commercial solidification techniques spanning a spectrum of technical complexity and cost. The most common methods include those based on cement or cement/pozzolanic materials. These materials, which are used in many solidification processes, make the technology appear simple and inexpensive. However, there are significant challenges to the successful application of this technique. The morphology and chemistry of the solidified waste forms are complex, specially when the waste streams used contain components other than the metals that are likely to be effectively immobilised. Also, the selection of the binder, depends upon an understanding of the chemistry of both the contaminants and the binder itself, to ensure efficient and reliable results. Nevertheless, a number of complex interactions are known to cause significant retardation on normal hydraulic reactions of cement-based materials, causing numerous and controversial problems.

In recent years there has been renewed interest in elucidating the binding mechanisms responsible for the fixation of waste species. Carbonation, which is known to affect a wide range of cementitious materials, is a phenomenon observed by many scientists and has received very little attention.

The aim of this work has been to investigate the effects of natural and accelerated carbonation on the development of mechanical and microstructural properties of solidified products as well as on the binding of metallic waste components. Particular emphasis was paid to examine the influence of different binders on the properties of carbonated solidified waste forms. The kinetics of the carbonation reaction was thoroughly examined, particularly when mix parameters such as binder/waste type and water content were varied.

An examination of the resulting products showed that carbonated solidified waste materials had improved mechanical properties and increased metal binding capacity, when compared to specimens cured in nitrogen or normal atmospheric conditions.

Microstructural analysis showed that large amounts of calcite where characteristics of carbonated samples. The increased formation of calcite as a result of carbonation appeared to be directly linked with the development of strength and enhanced metals fixation.

NMR and FTIR spectroscopy indicated that carbonation has a significant influence on the hydration of waste forms by increasing the degree of polymerisation of the silicate hydration phases, with a consequent acceleration of the hydration of the cement paste. Examination by SEM analysis confirmed an acceleration of C_3S hydration, typified by a de-calcified hydration rims and a matrix of dense calcite intergrowth infilling porosity. Some metals appeared to be incorporated in the silica-rich rims and others in the calcite rich matrix, suggesting precipitation of metal as both carbonates, silicates and complex double-salts.

An examination of the kinetic of the carbonation reaction revealed that the reactivity of the different cements was different in the presence of carbon dioxide, and that when metal wastes were added the susceptibility of the paste to react with carbon dioxide increased.

In general the results of this work indicate the potential of carbon dioxide for incorporation into the treatment of wastes during solidification. However, further work is necessary to establish the long-term performance of these carbonated waste forms as well as the behaviour of carbon dioxide upon different waste streams.

"The great tragedy of science: the slaying of a beautiful hypothesis by an ugly fact."

Thomas Huxley

To my late mother, Déa, whom I dearly miss

To my father, Francisco, with deep gratitude

To my husband, Jaime, with love

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NOTATION

BATNEEC	Best Available Techniques Not Entailing Excessive Cost
BPEO	Best Practicable Environmental Option
DoE	Department of the Environment
EA	Environment Agency (England and Wales)
EC	European Community
EPA 90	Environmental Protection Act (1990)
HMIP	Her Majesty's Inspectorate of Pollution
IPC	Integrated Pollution Control
USEPA	United States Environmental Protection Agency
WDAs	Waste Disposal Authorities
WRAs	Waste Regulation Authorities

CAC	Calcium Aluminate Cement
GGBS	Granulated Ground Blast Furnace Slag
OPC	Ordinary Portland Cement
PCBs	Polichlorobiphenyls
PFA	Pulverised Fuel Ash
PNAs	Polinuclearomatics
RHPC	Rapid Hardening Portland Cement
SF	Silica Fume
SRPC	Sulphate Resisting Portland Cement
WOPC	White Portland Cement

BEI	Backscattered Electron Imaging
DBI	Digital Backscatter Imaging
EDAX	Energy Dispersive analysis of X-Rays
FTIR	Fourier Transform Infrared Spectroscopy
ICP-AES	Inductively Coupled Plasma Emission Spectrometry
NMR	Nuclear Magnetic Resonance Spectroscopy
SEM	Scanning Electron Microscopy
TOC	Total Organic Carbon

UCS	Unconfined Compressive Strength
XRD	X-Ray Diffraction

The following cement chemists nomenclature is used in many sections of this work:

A	Alumina (Al_2O_3)
C	CaO
$\bar{C}$	Calcium carbonate ($CaCO_3$)
F	Fe_2O_3
H	H_2O (water of crystallisation)
S	Silica (SiO_2)
$\bar{S}$	Sulphate (SO_3)
C_3S	'Alite' or tricalcium silicate (Ca_3SiO_5)
C_2S	'Belite' or dicalcium silicate (Ca_2SiO_4)
C_3A	'Aluminate' or tricalcium aluminate ($Ca_3Al_2O_6$)
C_4AF	'Ferrite' or tetracalcium aluminoferrite (Ca_2AlFeO_5)
AFm	'Monosulphate' (C_4ASH_{12})
AFt	'Ettringite' ($C_3A.3CS.H_{32}$)
CH	'Portlandite' or calcium hydroxide ($Ca(OH)_2$)
C-S-H	Calcium silicate hydrate gel of variable composition
$C\bar{S}$	'Gypsum or calcium sulphate ($CaSO_4$)
C_3AH_6	'Hydrogarnet'

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CORRIGENDA

P. iii line 1 - "where" should be replaced by were

line 8 - "a" should be deleted

line 13 - "kinetic" should be kinetics

P. 19 Figure 1.2 - where is "retarder" should be replaced by retarded

P. 20 line 10 - instead of "griding" should be grinding

P. 22 last line - instead of "a" should be an

P. 30 line 17 - instead of "occuring" should be occurring

P. 47 line 9 - "needlelike" should be replaced by needle-like

P. 51 line 18 - "atteined" should be replaced by attained

P. 53 line 18 - "there" should be replaced by their

P. 69 line 3 - "a" should be replaced by an

P. 70 line 6 - instead of "X-ray intensity..." should be The X-ray intensity...

P. 71 line 6 - instead of "differs of" should be differs from

line 8 - instead of "a interferometer" should be an interferometer

line 9 - instead of "The FTIR process a number..." should be FTIR process has a number...

P. 74 line 7 and 11 - "quantitation" should be replaced by quantification

P. 75 line 12 - Appendix A instead of "Appendix 1"

P. 77 line 18 - binding instead of "biding"

P. 87 line 9 - instead of "dependant" should be dependent

P. 91 line 24 - "compounds" needs an apostrophe

P. 94 line 18 - delete "the" from ...the each of...

P. 100 line 9 - "consequence" should be replaced by consequent

P. 105 line 2 - "are" should be deleted and "appears" should be replaced by appear

P. 106 line 3 - "dependant" should be replaced by dependent

P. 107 line 21 - "derivated" should be replaced by derived

P. 127 line 20 - fixed instead of "fixing"

P. 139 The unit for frequency on Table 6.4 should be cm^{-1}

P. 151 line 5 - "asymetric" should be replaced by asymmetric

P. 152 line 15 - "correspondent" should be replaced by corresponding

P. 155 last line - instead of "a outbreak" should be an outbreak

P. 170 line 11 - instead of "might bound" should be might bind

P. 172 line 7 - instead of "adsorb" sould be adsorbed

P. 173 line 10 - instead of "living" should be leaving

P. 176 line 19 - instead of "cementitoius" should be cementitious

P. 177 line 25 - instead of "publicaly" should be publicly

P. 179 line 8 - instead of "general" should be generally

P. 185 line 6 - instead of "responsible of..." should be responsible for

P. 186 line 11 - instead of "this form..." should be this forms...

P. 186 line 21 - instead of "abundance" should be abundant

P. 188 line 4 - instead of "formed on the..." should be formed in the...

CHAPTER 1

INTRODUCTION

1.1 GENERAL BACKGROUND

Industrial activities indirectly give rise to very large quantities of waste each year and part of these residues have a major pollution potential and they require treatment before disposal.

In the UK the management of hazardous wastes was handled for many years on an "out of sight", "out of mind" principle and it was only the publishing of instances of indiscriminate or illegal disposal that brought the subject into the public domain. Ignorance of the amount of waste generated and where it was disposed of, precipitated some rapid legislation in the form of the "Deposit of Poisonous Wastes Act 1972". It was also about this time that solidification technology became available in the UK as a technique used to immobilise a variety of hazardous wastes thereby making them acceptable under land disposal requirements.

Solidification is an effective process in treating a variety of waste. It is flexible enough to accommodate mixtures of contaminants and economical enough to be used for large volumes of waste. Solidification technology involves physical and/or chemical encapsulation of waste species by a binder. These binders can be organic, such as thermoplastic and thermosetting polymers, and inorganic, such as cement (ordinary Portland cement) and pozzolan (pulverised fly ash). The inorganic binders are routinely used to solidify industrial sludges with low organic contents.

The practical application of Portland cement for the solidification of hazardous wastes has raised several questions regarding the long-term durability and stability of the waste compounds within the solidified matrix. It is known that a number of compounds found in wastes can have a detrimental effect on setting, strength and microstructure development of cement paste. A number of workers have been investigating the

chemical mechanisms for binding and incorporating hazardous constituents into solidification products, as a way of reducing these effects. However, data from several solidification applications reveals a lack of consistency in reporting which makes it difficult to interpret and compare results.

Furthermore, current public awareness coupled with a developing in EC legislation has led to rising standards and consequent increasing costs for methods of disposal. Two examples of environmental legislation in the UK that have a great impact are, first, the UK Environmental Protection Act of 1990, which has a clause known as the "Duty of Care" introduced a new principle into waste management. This makes the producers and disposers responsible for the fate of the waste, minimising its effect on the environment. Second, the Landfill Tax Regulation, that came into force in October 1996. This regulation has caused great alarm even by those favouring the idea in principle. The main impact for the solidification industries is that as bulk producers of industrial waste, they will face a sharp increase in their waste management overheads unless they succeed in finding recycling outlets (ENDS, 1995).

Therefore, there is a need for new processes and systems to treat difficult hazardous wastes prior to landfill. The present work investigates the influence of carbonation on the properties of solidified wastes through a detailed literature and laboratory study of the kinetics of carbonation reactions and their influence on the hydration, microstructural development and nature of bonding of different waste species within hydrated cement-based systems.

In this Chapter, a review of the published literature concerning the basis for cement-based solidification, including legislation and control as practiced in the UK, is presented. This is followed by a brief review of the carbonation of concrete related to porosity, strength, permeability and hydration chemistry. A detailed summary of recent laboratories studies of carbonation on metal-doped Portland cement paste is also given. The chapter concludes with an outline of the current work and the main objectives.

1.2 HAZARDOUS WASTE MANAGEMENT: LEGISLATION AND CONTROL

1.2.1 General

The hazardous waste management industry currently faces a number of challenges, in Europe and elsewhere. Principal amongst these is the drive for tighter controls and higher standards at landfill sites and other treatment plants. Much of this pressure originates within the European Community (EC), and in addition to legislative pressures, come the industries that are moving to improve their quality and environmental standards (British Standards, 1987 and 1992). Other pressures come from investors, insurers and the general public.

The legislation and practices currently used in the UK and Europe, relevant to the context of this work, are summarised below.

1.2.2 European Legislation

The control of waste of all types has come under EC legislation, the purposes being to prevent the distortion of trade which might result from varying standards in different member states and to protect the environment within the community. The usual instrument employed to achieve these results is the directive, which sets out the objectives to be achieved but leaves it to the individual states to implement specific methods of so doing.

Framework Directives

A directive of particular importance is the 1975 framework directive on waste, 75/442/EEC, which called for the prevention and recycling of waste, required member states to establish competent authorities to ensure waste disposal without harm to the environment and human health (Croner's Waste Management, 1991). This directive was amended in 1991, (91/156/EEC) by expanding the original legislation, defining a waste and listing 16 categories of wastes subject to control. Part II of the UK Environmental Protection Act 1990 (EPA) was designed to implement many of the provisions of these directives (Price, 1993).

Specific Measures Relating to Hazardous Waste

The first piece of EC legislation aimed directly at hazardous waste was the 1978 directive on toxic and dangerous waste (78/319/EEC) (Croner's Waste Management, 1991). This required controls on the dumping of wastes containing any of 27 specified substances at potentially harmful concentrations, and imposed controls on packing, storage, treatment and transport of such wastes. Waste minimisation and recycling were also goals of this directive.

The 1978 directive was intended to be superseded at the end of 1993 by the hazardous waste directive (91/689/EEC) but continuing debate over definitions of waste has resulted in delay (Price, 1993). This directive will define a wider range of wastes and prohibit the mixing of hazardous waste except where mixing is a genuine part of the disposal operation (ENDS, 1994).

Transfrontier Shipment of Waste

Directive 84/431/EEC on the transfrontier shipment of hazardous waste, (subsequently amended by directive 86/279/EEC) was designed to regulate the movement of waste of all types across the community's borders (Macrory, 1991). Later on, in 1992, the Council of Environmental Ministers of the EC agreed a Regulation on the supervision and control of shipment of waste within, into and out of the EC (259/93/EEC) which will enable the 12 member states of the EC, including UK to ratify the Basel Convention of 1989 - convention of transboundary movements of hazardous wastes and their disposal (Encyclopedia of Environmental Law, 1993).

Landfill

Landfill practices are affected by the directive 80/68/EEC on the protection of groundwater against pollution by dangerous substances. It requires that certain materials (List I subs.) should not be discharged to groundwater, on List II substances require investigation prior to discharge (Price, 1993).

Eventually the standards for operation and pollution prevention at landfill sites are to be harmonised throughout the EC Landfill Draft Directive (1993). This directive purposes

that hazardous waste is defined in terms of the constituents of leachate arising from it, as illustrated in Table 1.1, below.

Table 1.1: Leachate criteria for hazardous waste

Parameters	Range	Parameters	Range
pH	4-13	fluoride	10-50 mg/l
TOC	40-200 mg/l	ammonium	0.2-1.0 mg/l
arsenic	0.2-1.0 mg/l	chloride	1.2-6.0 g/l
lead	0.4-2.0 mg/l	cyanide [1]	0.2-1.0 mg/l
cadmium	0.1-0.5 mg/l	sulphate [2]	0.2-1.0 g/l
chromium	0.1-0.5 mg/l	nitrite	6-30 mg/l
copper	2-10 mg/l	AOX [3]	0.6-3.0 mg/l
nickel	0.4-2.0 mg/l	solvents [4]	0.02-0.10 mgCl/l
mercury	0.02-0.1 mg/l	pesticides [4]	1-5 µg/l
zinc	2-10 mg/l	lipoph.sub.	0.4-2.0 mg/l
phenols	20-100 mg/l		

Note: (1) Readily released; (2) If possible < 500 mg/l; (3) Adsorbed organically-bound halogens; (4) Chlorinated.

1.2.3 UK Legislation

Legislation to control hazardous waste disposal in the UK was first introduced in 1972. It followed a number of incidents involving the illicit disposal of drums containing cyanide residues on waste grounds used by children. An emergency bill was introduced by the government in the form of the Deposit of Poisonous Wastes Act 1972.

Control of Pollution Act 1974

This is a wide-ranging enabling act, under which regulations have gradually been introduced over the last 15 years to cover various aspects of the control of waste management. Most types of waste (e.g. municipal, commercial and industrial) are defined as controlled wastes and any site handling them has to be licensed and requires planning consent (Price, 1993).

Special Wastes

Additional measures adopted to control more dangerous wastes are in the Control of Pollution (Special Wastes) Regulations 1980 which repealed the Deposit of Poisonous Waste Act 1972. 'Special Wastes' are defined by means of an inclusive list and for a waste to be special, it has to contain or consist of one or more of the substances listed and, by virtue of this, be flammable, a prescription-only medicine or dangerous to life.

The special waste regulations have been widely criticised both because of their definitions, which was only concerned with human health and did not consider the effects of the waste on the environment in general, and the way in which they operate - the record keeping by WDAs (Waste Disposal Authorities). In an attempt to deal with the definitions of special wastes, and reconcile the regulations with the EC requirement to protect the environment, a consultation paper was issued in 1995 (DoE, 1995) in which a new definition of special waste was proposed. A fee must now also be paid when pre-notification is made, to recover the supervisory costs incurred by WRAs under the regulations. Many of the changes derive from the Directive 91/689/EEC on hazardous waste, and council decision 94/904/EC. Others arise from the review of the 1980 Regulations and proposals published in 1990. The new Special Waste Regulations came into effect on 1995 (DoE, 1995). They revoke and replace previous special waste regulations, and also regulations on landed ships' wastes.

The Environmental Protection Act 1990

The Control of Pollution Act 1974, however, had considerable weaknesses, for example a license was not necessarily required before opening a site. The Environmental Protection Act (EPA) of 1990 sought to overcome these. This act sets up registration schemes for waste carriers, tighter licensing, higher fines, the necessity for suitably qualified site operators and supervision of closed sites, in time these closed sites receiving a "Certificate of Completion".

An important clause in the EPA 1990 is known as the "Duty of Care". The duty can be viewed as requiring everyone, i.e. producers, carriers, treaters, disposers, stores and brokers, to demonstrate that all reasonable steps have been taken to prevent the escape of any waste under their control, prevent the unauthorised or harmful disposal of waste

by third parties, ensure waste is passed on only to an authorised person (i.e. registered carrier, holders of waste management licences operating treatment or disposal facilities, or exempted persons), ensure the waste is properly contained and described to the authorised person receiving the consignment (Young et al., 1993).

A new legislative principle also introduced by the EPA is that of integrated pollution control (IPC), which seeks to minimise the environmental effects of all media of scheduled processes. It provides a mechanism and a legal basis for looking at the impact which a process as a whole has on the environment as a whole, balancing the imperative of protecting the environment against the reality that this protection has a financial cost (Biggs, 1995):

* IPC takes a holistic approach, ensuring that substances which are unavoidable released to the environment are released to the medium in which they will cause least damage. The ability of the receiving environment to absorb the pollution is assessed. The principle of the Best Practicable Environmental Option (BPEO).

* IPC embodies the precautionary principle: prevention is better than cure. Therefore operators are required to use the best available techniques not entailing excessive cost (BATNEEC) to reduce emissions.

* The regulatory process from application, through authorisation, to regular returns of the results of monitoring releases to the environment, and, where appropriate, to the enforcement action taken by Her Majesty's Inspectorate of Pollution (HMIP), is open to public scrutiny and comment.

At this point it should be noted that as from 1 April 1996, much of the responsability for the regulation of pollution control was transferred from the HMIP to the Environment Agency in England and Wales and the Scottish Environment Protection Agency (SEPA).

Proposals for establishing independent environment agencies in the UK were published for consultation in 1991 and confirmed in July 1992. The Agencies, which have formally taken over their pollution control and other functions, were established by the *Environment Act 1995*, Part I, which received the Royal Assent on 19 July 1995 (NSCA Pollution Handbook, 1996).

EC Directives and Corresponding UK Legislation

Table 1.2 shows some of EC directives implemented in the UK and their corresponding UK statutes (Crone's Waste Management, 1991).

Table 1.2: EC Directives implemented in the UK and their corresponding UK statutes

Subject	EC Directive References	UK Statute
Used oils	75/439, 87/101	Collection and Disposal of Waste Regulations 1988 (SI No 819) - arguably only a partial implementation.
Waste framework directive	75/442	Control of Pollution Act 1974.
PCBs and PNAs	76/403, 91/689	Control of Pollution (Special Waste) Regulations 1980 (SI No 1709). New special waste Regulations (SI 1995/...).
Dangerous substances discharged to the aquatic environment (a number of daughter directives give standards for specific substances).	76/464	Trade effluents (Prescribed Processes and Substances) Regulations 1989 (SI No 1156) as amended by SI 1990 No 1629. Surface Waters (Dangerous Substances) (Classification) Regulations 1989 (SI No 1709).
Toxic and Dangerous Waste	78/319	Control of Pollution (Special Waste) Regulations 1980 (SI No 1709).
Protection of groundwater against pollution caused by certain dangerous substances	80/68	Water Act 1989 (see also DoE circular 20/90 of 29.10.90).
Supervision and control within the EC of the transfrontier shipment of hazardous waste	84/631, 85/649, 86/279, 87/112, 93/259	Transfrontier Shipment of Hazardous Waste Regulations 1988 (SI No 1562).

Other Statutory and Non-Statutory Controls

Statutory Controls

Hazardous wastes are subject to a range of controls applying to any form of industrial activity. *The Health and Safety at Work Act 1974* complied with in order to protect the workforce from undue hazard by virtue of their employment there. *The National Rivers Authority* (NRA) was a statutory consultee. It was the body responsible for ensuring that groundwater was protected. The NRA was expected to exert its influence via the planning process and through the waste management licensing procedure. From 1 April 1996, the Environment Agency has assumed all the responsabilities of the NRA as well as responsability for Integrated Pollution Control and waste regulation.

Non-Statutory Controls

A range of voluntary controls has been adopted or is under consideration by waste management companies. Some of these controls are: British Standards, eco-audits, codes of practice, investment pressures, Royal Commission on Environmental Pollution, pressure groups ('green' movements).

1.3 HAZARDOUS WASTE TREATMENT TECHNIQUES AND DISPOSAL OPTIONS

1.3.1 Hazardous Waste Arising

Completely reliable data on hazardous waste arisings, within the UK and elsewhere, are difficult to come by for several reasons. Firstly, an appropriate definition for the UK is difficult because the definition of hazardous waste varies from country to country. A second problem is that of data collection, where different countries collect data on waste arisings in different ways and with varying degrees of thoroughness.

In the UK, in 1988/89 approximately 4.5 million tonnes of hazardous wastes were produced (DoE, 1991) and it was estimated that over 80% of these were directly sent to landfill without pre-treatment (Denner, 1991). 1.8 million tonnes of the hazardous wastes generated were 'special'. Table 1.3 shows the arising of special wastes in the UK

(Price, 1993). Also important is that in addition to those wastes generated within the UK varying amounts are imported for disposal. In 1990/91 the figure was slightly under 44,000 tonnes as shown in Table 1.4.

Table 1.3: Special waste arisings , UK, 1986/87 - 1990/91

	T x 10^3				
	Total UK	**England**	**Wales**	**Scotland**	**NI**
1986/87	1,629	1,500	94	30	5
1987/88	2,141*	2,070	-	59	12
1988/89	1,905	1,762	60	66	17
1989/90	2,315	2,146	80	71	18
1990/91	2,542	2,352	76	94	20

Scottish data are on calendar year basis.

* excluding Wales

Table 1.4: Disposal routes for imported hazardous wastes, England and Wales, 1990/91

Route	Tonnage	%
Physical and chemical treatment	25,493	58
Incineration	12,746	29
Solidification	3,077	7
Other methods (including direct landfilling, recycling and reprocessing)	2,637	6
Total	**43,953**	**100**

1.3.2 Hazardous Waste Disposal Routes

The main disposal routes available in the UK are (Price, 1993):

a) Landfill - 70%

b) Physical/chemical treatment - 15%

c) Marine dumping - 10%

d) Incineration - 5%

The choice of disposal route is influenced and constrained by the following factors:

a) Legislative requirements and restrictions

b) Cost

c) Availability of suitable disposal facilities

d) Potential environment impact of the waste

e) The possibility of criminal or civil liability in the future

Sea disposal is being phased out as a result of the Oslo and North sea 1992 convention. Incineration is an expensive waste management option, suitable mainly for wastes of high calorific values. This option is sophisticated, needs efficient incinerators to limit both the quantity and type of air emissions and the initial capital investment is higher (Wentz, 1989). Another point is that recent draft legislation from the EC (Landfill Draft Directive, 1993) imposes strict emission standards for particulates, toxic metals and dioxins.

Direct landfilling predominates. It is generally the cheapest disposal option for solid wastes, but for liquids it involves transportation and disposal costs which are in total considerably higher than the costs for disposal to sewer. An interesting survey was produced by Frank Graham Consulting Engineers, where a recent official estimate of future landfill clean-up costs has been challenged (ENDS, 1992). The findings suggest that one in six British landfills have caused water pollution or gas migration incidents, as illustrated in Figure 1.1, and that remedial costs of several hundred thousands pounds or more are not uncommon.

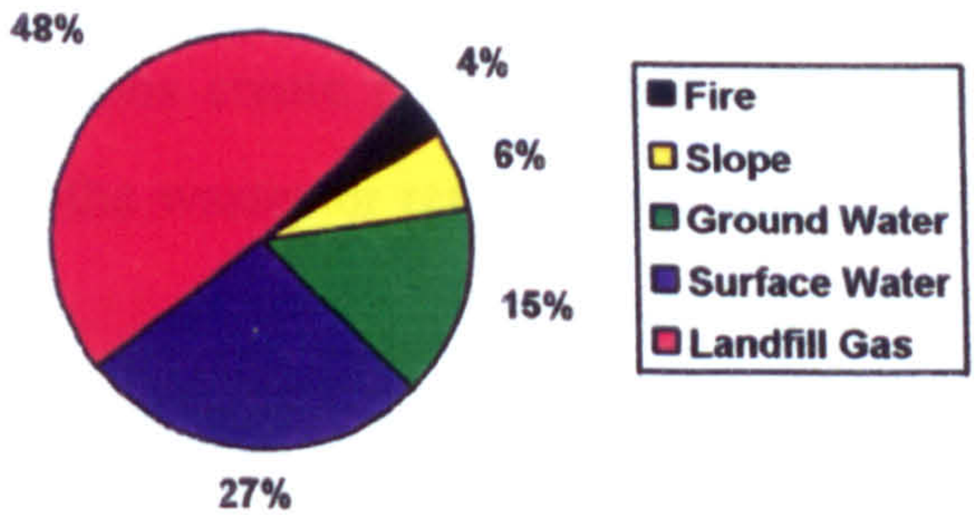

Figure 1.1: Category of incidents or failures involving landfills (ENDS, Nov. 1992)

Therefore, despite a very large number of wastes are allowed to go to landfill, changes in the present legislation (EC landfill directive), may require wastes to be pre-treated.

At present, hazardous wastes are disposed in mono and co-disposal sites, with the latter being the subject of some recent debate (ENDS, 1993 and 1996). The UK considers the co-disposal practice "vital" and provides an "environmentally sound" disposal route for 2.8 million tonnes of industrial waste annually. In the UK there are presently about 100 co-disposal sites licensed to take special wastes and whose disposal practices are regulated by the Department of Environment

Also the impact of the proposed EC Landfill Directive, together with other convergent legislative pressures, will produce major changes in European waste management practice in the 1990's (Perry et al., 1992). Some major features of these change will be:

- much greater emphasis on waste minimisation or even elimination at source, together with active exploration of re-use opportunities.
- steadily increasing costs for landfill disposal.
- greater awareness of landfill as a scientifically-based disposal option, with consequent need for greatly increased professionalism in management.
- greater economic incentives for the expansion and development of existing non-landfill alternatives, such as incineration and solidification and for the re-evaluation of minor existing technologies.
- continuing impetus for research and development in new technologies.

1.3.3 Hazardous Waste Treatment Techniques

Most manufacturing operations create products that will ultimately need to undergo treatment to either destroy the wastes or render them harmless to the environment. The objectives of treatment are:

i) To reduce disposal costs
ii) To comply with legislative requirements
iii) To implement an environmental policy
iv) To form part of a waste minimisation or in house recycling programme.

There are numerous treatments applicable to hazardous wastes that can typically be categorised as thermal, physical, biological and chemical. Combinations of these treatment technologies are often utilised to develop the most cost-effective and environmentally acceptable solutions to waste management problems.

Thermal Treatment

Most hazardous wastes consist of carbon, hydrogen and oxygen, other compounds such as halogens, sulphur, nitrogen and heavy metals are also often present. If the waste molecules can be destroyed or reduced to carbon dioxide, water, and associated inorganic substances, the organics should be rendered harmless (Wentz, 1989). For these reasons, thermal destruction has generally become recognised as a preferred treatment technology in the management of hazardous wastes.

Physical Treatment

Physical treatment involves a wide variety of separation techniques that have been commonly practised throughout industry for decades (Metcaff and Eddy, 1979). Whenever a waste containing liquids and solids must be treated, physical separation must be considered first, if a cost-effective method and efficient management is required (Wentz, 1989). Physical processes for the separation of liquids and solids include screening, sedimentation and clarification, centrifugation , flotation, filtration, sorption, evaporation and distillation, stripping and reverse osmosis.

Biological Treatment

Biological treatment can be an efficient, cost-effective way to remove hazardous substances from contaminated wastewater and groundwater, landfill leachate and contaminated soil (Grady and Lim, 1980). The microbes for biological treatment may be classified as heterotrophic or autotrophic, depending upon their source of nutrients. Exist two types of systems in the biological treatment: aerobic system and anaerobic system.

Chemical Treatment

Chemical treatment involves the use of reactions to transform hazardous waste streams into less hazardous substances. It can be employed to produce useful by-products and residual effluents that are environmentally acceptable (Tedder et al., 1991).

Types of chemical treatment include solubility, neutralisation, precipitation, coagulation and flocculation, oxidation and reduction, colour removal, disinfection, ion exchange and solidification processes.

A widely used method for the disposal of solid wastes is cement-based solidification technique. This technique is widely used in the US and Japan and typically involves the treatment of inorganic, heavy metal bearing wastes. The process involves the addition of binders such as Portland cement, cement kiln dust, fly ash or similar reagents. The resulting solidified products are generally low in permeability and are often used for land reclamation. It is claimed to retain the toxic components of the treated wastes and thus minimises any potential for the contamination of ground or surface waters, being the subject of the present study.

1.4 SOLIDIFICATION TECHNOLOGY

1.4.1 General

Solidification has been used to a lesser or greater extent in most industrialised nations to immobilise a variety of hazardous wastes. Solidification process for the stabilisation and solidification of toxic and hazardous wastes have been available for nearly 25 years, with the first UK patent being granted in 1974 (Chappel, 1974).

Solidification treatment is designed to reduce the mobility of the toxic waste element thereby making the waste acceptable under land disposal requirements. It is an economical process for the disposal of many types of hazardous wastes (Pojasek,1979 and Conner, 1990).

So far, no one solidification process has been developed which is optimal or even applicable to every type of hazardous wastes. Binders often consist of Portland cement (Ordinary Portland Cement, OPC) or OPC plus fly ash, kiln dust, other pozzolanic and industrial by-products. Sometimes polymers, by themselves or in various combinations, are used (Roy et al., 1992).

In principle, cement-based solidification rely upon the formation of a silicate or alumino silicate matrix within which the waste constituents are incorporated (Sollars et al., 1989). When properly prepared, the solidified product should allow only a very gradual release of toxic components into the environment (Anderson et al., 1979).

1.4.2 History of Process Development

Solidification processes have developed from man's attempt to better navigation or transportation. In ancient times (3,000 B.C.) the Chinese Dschou dynasty had customs for road construction. The Roman port of Cosa (2nd century B.C.) utilised mortar called pozzolana for harbour protection. It is of interest that these harbour structures of Cosa still exist, indicating long-term durability. Pozzolana was volcanic tuff obtained from the neighbourhood of Pozzol. Roman roads (e.g. Appian Way) were "stabilised" with lime for better properties (Barth, 1990). Concretes today are based on an 1824 patent covering limestone and clay for mortar (Popovics, 1981).

In the United States, road construction methods were refined to include stabilisation with lime. Early research and development work on road stabilisation and durability was performed by the US Army Corps of Engineers. This technology has seen extensive use for the remediation of contaminated land. The USEPA estimate that 28% of remedial actions undertaken in 1992 involved solidification. "Innovative" technologies were used in 44% of cases involving approximately 9.8M cubic yards of soil (USEPA, 1993).

There is little literature relating to solidified products that have been disposed of in the UK. Solidified products have historically been sent to landfill either dedicated for that use or co-disposed (Hills, 1993). In the UK, there have been three major commercial solidification operations using cement. One plant, based on a patented cement/sodium silicate process, "Chemfix Process", was operated during the 1970's/1980's, but is

currently not operational. The two other processes are based on the "Stablex Process" and involve the use of PFA as a cement replacement material. One plant is based in the West-Midlands and commenced operations in the mid-1970's, although it is understood it is currently not operational (Gans, 1990). The second plant, in Essex, came on stream in January 1978 and closed down on October 1995. This plant accepted wastes predominantly contaminated with heavy metals. Sources include electroplating, metal refineries, galvanizers, metal finishing, etc.

Some doubts about the suitability of cement-based solidification for some wastes were reported as long ago as 1983 (ENDS, 1983) and recently there has been some alarming news of failed solidified wastes in the English Midlands (ENDS, 1988; ENDS, 1989; ENDS, 1990). There is also some difficulty in treating certain particular waste streams, like some slurries associated with nuclear processing at Sellafield (Webb, 1993).

1.4.3 Definition and Types of Solidification Processes

Solidification *refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity.* The encapsulation may be of fine waste particles (micro encapsulation) or of a large block or container of wastes (macro encapsulation). Solidification does not necessarily involve a chemical interaction between the wastes and the solidifying reagents, but may mechanically bind the waste into the monolithic. Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching and/or by isolating the wastes within an impervious capsule (Conner, 1990).

Solidification technology can be broken into the following six major categories based on binder type (Weitzmann, 1990):

1) Cement-based binders - success based on the provision of high pH, reduction in surface area to volume ratio, and decrease in permeability.

- Portland cement
- Cement kiln dust
- Fly ash mixtures

2) Lime based binders - depends on the reaction of lime with fine grained siliceous material and water to produce a hardened material, best for inorganic wastes.

- Lime
- Lime kiln dust
- Mixtures of fly ash and lime

3) Absorbents - are generally not considered to be an acceptable method of solidifying liquids. While certain metals, an even, possibly, some organics may have their leachability diminished by absorption on solids.

- Hydro and organophillic clays
- Wood chips, sawdust, rice hulls

4) Thermoplastic materials - they have been used to encapsulate radioactive wastes.

- Asphalt bitumen
- Thermoplastic polymer

5) Thermosetting polymers - they have also been used to encapsulate solidified radioactive wastes.

6) Vitrification - is a process by which the waste is melted into a solid, rocklike material.

Cement-based binders are in general the most widely used of the above.

1.5 CEMENT-BASED PROCESSES

The principle of cement-based solidification appears very simple. The technology involved is low, the materials required are available locally, i.e., they are mass-produced and generally inexpensive compared with energy-intensive treatment processes such as, vitrification and incineration (Mean et al., 1995).

Many types of cement have been used for a variety of purposes, but only those classified as Portland cement, which are primarily composed of anhydrous calcium silicate, have seen substantial use in cement-based solidification (Conner, 1990). Other types of cement, such as calcium aluminate cement, have not been used extensively for solidification, primarily because of their high cost and, in respect of CAC's some fundamental misconceptions concerning building collapses that occurred in the 1970's. Cement-based systems are often used for the treatment of liquid, sludge and solid wastes. The technical basis for the success of the cement-based techniques is a reduction in the surface area to volume ratio, the provision of a high pH rendering the metals insoluble, and a decrease in permeability in the sludge mass.

The following section discusses the main cements and replacement materials used during solidification and their applicability to waste/cement systems.

1.5.1 Portland Cement

1.5.1.1 General

Portland cement is an ubiquitous material. It has many applications where it is expected to endure aggressive environments and at the same time maintain a high level of performance.

Portland cement is made by heating a mixture of limestone and clay to a temperature of about 1450°C, where partial fusion occurs, and nodules of clinker are produced. the clinker is mixed with a few percent of gypsum and finely ground to make the cement (Taylor, 1990). The main constituents of Portland cement and their hydration products are given in Figure 1.2 (note that the box size represents relative proportions of constituents).

The basic constituents of the most widely used type of Portland cement, ordinary Portland cement (OPC), are: tricalcium silicate (C_3S* approx. 50%); dicalcium silicate

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* Where C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, $\bar{S}$ = SO_3 and H = H_2O in cement chemists nomenclature.

(C_2S approx. 25%); tricalcium aluminate (C_3A approx. 10%); alumino-ferrite phase (C_4AF approx. 10%) and gypsum ($C\bar{S}H_2$ approx. 2%).

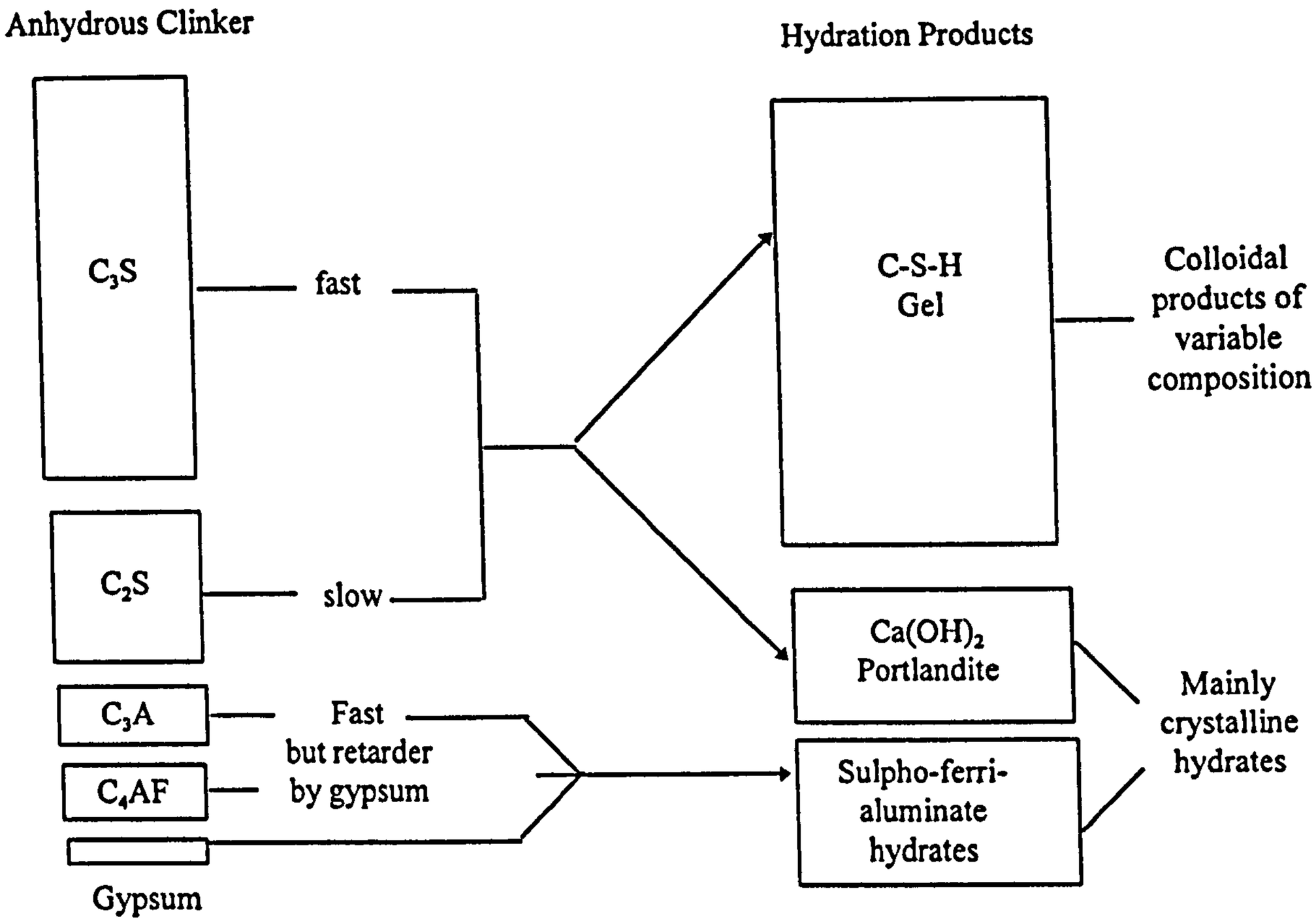


Figure 1.2: Diagram representing the main constituents of Portland cement and their hydration products (after Lea, 1970)

1.5.1.2 Types of Portland Cement

There are many types of Portland cement, however, they all have one feature in common: they are obtained from silica, alumina, and iron oxide bearing materials burnt at a clinkering temperature (i.e. below the point if complete fusion). The great majority of Portland cements made throughout the world are designed for general constructional use. Specifications are based partly on chemical composition or physical properties such as specific surface area, and partly on performance tests, such as setting time or compressive strength developed under standard conditions.

Table 1.5 gives the main types of Portland cement and the ASTM composition limits for some of these cements (Neville, 1981). The cements chosen for this work are marked

(*). Those cements are the most common Portland cements and they have a varied chemical composition, which is important for this research.

Table 1.5: Main types of Portland cement and ASTM specification C/50 - 78a: compound composition limits for cement

British Description	ASTM Description	C_3S Max.	C_2S min.	C_3A max.
Ordinary Portland (*)	Type I	-	-	-
Rapid Hardening Portland (*)	Type III	-	-	15
Extra Rapid Hard. Portland				
Ultra High Early Strength Port.				
Low heat Portland	Type IV	35	40	7
Modified cement	Type II	-	-	8
Sulphate resisting Portland (*)	Type V	-	-	5
Portland Blast-Furnace	Type IS	-	-	-
White Portland (*)		-	-	-
Portland-Pozzolana	Type IP Type P	-	-	-
Slag cement	Type S	-	-	-

Ordinary Portland cement (OPC) is by far the most common cement in use in the US and in the UK. Over the years, there have been some changes in the characteristics of OPC. In particular, modern cements have a higher C_3S content and a greater fineness than 40 years ago (Neville, 1981).

Rapid hardening Portland cement develops strength more rapidly, and should therefore be correctly described as high early strength cement. The increased rate of gain of strength of the rapid hardening cement is achieved by a higher C_3S content and by finer griding of the cement clinker.

Destructive expansion from reaction with sulphates can occur not only if the latter are present in excessive proportion in the cement, but also on exposure of concrete to sulphate solutions. The reactions involve C_3A with gypsum, forming calcium sulphoaluminate and a base exchange between calcium hydroxide and the sulphates.

These reactions are known as sulphate attack. The remedy lies in the use of cement with a low C_3A content, and such cement is known as sulphate-resisting Portland cement.

White Portland cements are made by increasing the ratio of Al_2O_3 to Fe_2O_3, and thus represent the opposite extreme in composition to sulphate resisting Portland cements.

1.5.1.3 Hydration Reactions of Portland Cement

Portland cement is a mixture of a number of minerals, the most important being calcium silicates, calcium aluminates, and iron oxide. The fundamental chemical reactions of Portland cement are shown on Table 1.6 (Weitzmann, 1990).

Table 1.6: Fundamental chemical reactions of Portland cement

$2(3Ca.SiO_2)$	+	$6H_2O$	→	$3CaO.2SiO_2.3H_2O$	+	$3Ca(OH)_2$
Tricalcium Silicate		Water		Tobermorite gel		Calcium hydroxide
$2(2CaO.SiO_2)$	+	$4H_2O$	→	$3CaO.2SiO_2.3H_2O$	+	$Ca(OH)_2$
Dicalcium silicate		Water		Tobermorite gel		Calcium hydroxide
$4CaO.Al_2O_3.FeO_3$	+	$10H_2O$	+	$2\,Ca(OH)_2$	→	$6CaO.Al_2O_3.FeO_3.12H_2O$
Tetracalcium aluminoferrite		water		Calcium hydroxide		Hexacalcium aluminoferrite
$3CaO.Al_2O_3$	+	$12H_2O$	+	$Ca(OH)_2$	→	$4CaO.Al_2O_3.13H_2O$
Tricalcium aluminate		water		Calcium hydroxide		Tetracalcium aluminate hydrate

The rate of these reactions is varied and is dependent upon, for example, the phase composition, temperature and presence of acceleratory or retarding agents. The normal reaction rates of the clinker phases can be arranged in the following order: (Jennings, 1983; Young, 1981; Taylor, 1990)

$$C_3A > C_3S > C_4AF > C_2S$$

However, the impure alite and belite phases present in Portland cement react faster than the pure phases. Other factors such as the particle shape and particle size distribution also influence the reactivity of the cement. The influence of these factors on the rate of

hydration are considered in more detail by Soroka (1979), Scrivener (1984) and Taylor (1990).

The hydration chemistry is dominated by the calcium silicate phases and these provide the main sources of strength development in the cement paste (Poon, 1985).

Several distinct stages in the hydration of tricalcium silicate have been identified (Jennings et al., 1978; Birchall et al., 1978; Birchall et al., 1980) and are given in Figure 1.3.

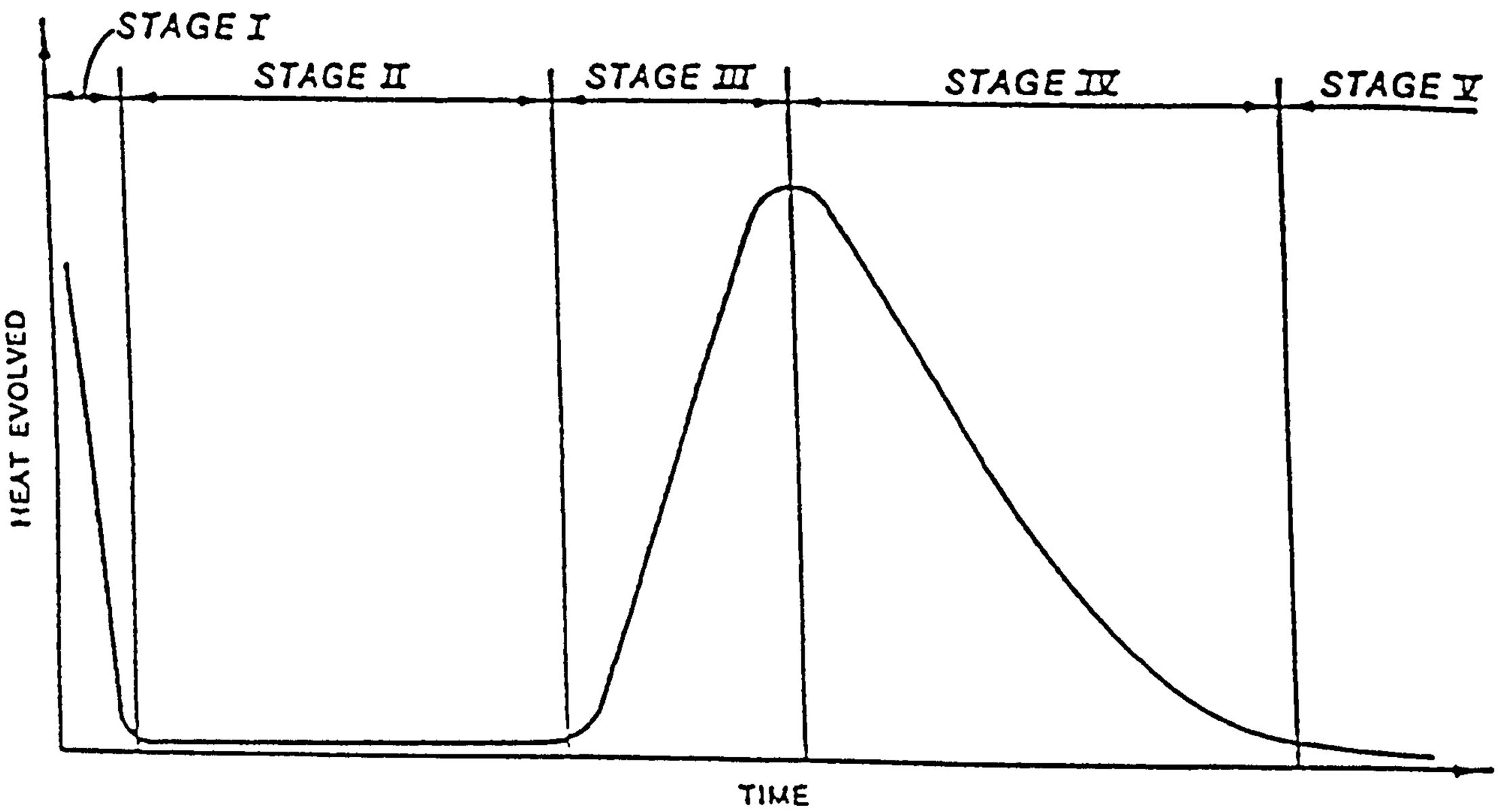


Figure 1.3: Heat liberation curve for the hydration of tricalcium silicate, determined by isothermal conduction calorimetry

Stage I: when OPC is dispersed in water, calcium ions are rapidly leached from the solids to form a solution of mainly $CaO.H_2O$.

Stage II: The $CaO.H_2O$ react with silicic acids on the surface of the cement grains to form a gelatinous semi-permeable membrane of C-S-H around the cement grains. A osmotic pressure inside the membrane increases.

Stage III: The osmotic pressure inside the membrane causes it to rupture with the development of new C-S-H. This stage is also characterised by the initial $CaO.H_2O$ crystallisation and by the transformation of C-S-H gel which exposes additional surface area of the anhydrous particles.

Stages IV and V: Are characterised by deceleration of the diffusion controlled reactions.

The reaction mechanisms proposed for the hydration reactions are considered in greater detail by Jennings (1979), Skalny (1980), Gartner et al. (1989) and Taylor (1990). The changes in morphology associated with the early hydration period are covered by Lea (1970), Jennings (1979), Scrivener (1984, 1989) and Taylor (1990). More recently, Diamond and Bonen (1993) showed a new interpretation for the morphological features of hydrated Portland cement paste, where the microstructure is seen to consist of distinct grains (phenograins) set in a cellular groundmass. They also carried out an Energy Dispersive X-Ray Analysis (EDXA) for the cement paste attributing minor ionic substitutions for the C-S-H gel phase, and an extensive occurrence of intimate mixtures of C-S-H gel with the other components below the scale of scanning electron microscopy (SEM) observation (Bonen and Diamond, 1994).

1. 5.2 Calcium Aluminate Cement

1.5.2.1 General

Calcium aluminate cements (CAC) are manufactured in many countries, either by fusion or sintering of bauxite and calcareous raw materials. The mineralogy of CAC differs from that of Portland cements, which are based on calcium silicates, rather than calcium aluminates. The series of calcium aluminate compounds using cement chemistry notation are:

$$C_3A,\ C_{12}A_7,\ CA,\ CA_2 \text{ and } CA_6$$

Of these the hydraulically active compounds found in CAC are, $C_{12}A_7$, CA, CA_2 , where CA is by far the major phase present - 50% or more by weight. The quantities of

the compounds present in cement are generally not determined direct but are calculated from the known proportions of the oxides. Table 1.7 gives the range of typical percentage of the oxides present in CAC (Neville, 1975).

Table 1.7: Typical oxide composition of CAC made in various countries

Country	CaO	Al_2O_3	SiO_2	Fe_2O_3	FeO	TiO_2
UK France Spain	35 - 39	37 - 41	3½ - 5½	9	6	1½ - 2
Germany	38 - 42	44 - 51	5 - 8	0 - 1	½ - 2	1 - 2
USA	35 - 39	37 - 41	8 - 10	4 - 6	4 - 6	1½ - 2

1.5.2.2 Properties of Calcium Aluminate Cement

Rapid hardening

CAC's are slow setting (i.e. about the same as Portland cements) but very rapid hardening. Strengths equivalent to the long term design strength are reached within few hours (typically 40MPa after about 6 hours) (Taylor, 1990).

Low Temperature Concreting

The rapid hydration of CAC is accompanied by a release of the heat, which, although of the same order of magnitude as Portland cement, is released within hours and not days. This leads to a substantial increase in the temperature of the concrete, which may be turned to advantage for concreting in extremely cold conditions (Montgomery et al., 1993).

High Temperature Resistance

CAC's are also widely used in refractory concretes for their high temperature resistance, up to 2000°C.

Resistance to Chemical Attack

The chemistry of CAC's is fundamentally different from that of Portland cements. No portlandite $Ca(OH)_2$ is formed during hydration which means that concretes made from CAC resist attack by many substances which are aggressive to OPC e.g. sewage

(sulphuric acid), dilute inorganic and organic acids, sulphates, chlorides, sea water, oils, fats, etc. (Montgomery et al., 1993). The aluminium hydroxide gel (Al_2O_3.aq), which is produced during hydration is, however, attacked by caustic alkalis such as sodium and potassium hydroxide, and HAC is, therefore, not resistant to such agents (Neville, 1975).

Conversion of CAC

An important property of CAC is the phenomenon known as conversion. It was mentioned that monocalcium aluminate CA is the main cementitious compound in CAC. In the presence of water, at low temperatures (<20°C), chemical reactions take place producing first alumina gel, and a few hours later CAH_{10} is formed. Some C_2AH_8 is also formed but is rarely present in excess of 1-2%. If, however, hydration proceeds at a higher temperature, such as 45°C, the main product formed is C_3AH_6. The important point is that CAH_{10} and C_2AH_8 have pseudo-hexagonal symmetry while C_3AH_6 is cubic and at higher temperatures only the cubic form can exist; at room temperature either can, but the hexagonal crystals spontaneously convert to the cubic form. So, conversion is the transformation of the meta-stable hydrates CAH_{10} and C_2AH_8 to stable C_3AH_6 (Midgley, 1975).

$$3CAH_{10} \rightarrow C_3AH_6 + 2AH_3 + 18H \qquad \text{(Eq. 1.1)}$$

$$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H \qquad \text{(Eq. 1.2)}$$

Rashid et al. (1992) found that reaction 1.1 does not occur directly but passes via C_2AH_8 .

Conversion is accompanied by the release of bound water, which increases the porosity of the concrete and causes a certain loss of strength. The increase in porosity and hence the decrease of strength are governed mainly by the water/cement ratio of the concrete and is therefore limited and quantifiable (Montgomery et al., 1993).

1.5.2.3 Hydration of Calcium Aluminate Cement

CAC is a hydraulic cement, i.e., it sets and hardens by chemical reactions with water and remains stable in the presence of water.

The hydration of CA, which, of the compounds present in CAC, has the highest rate of strength development, results in the formation of CAH_{10}, a small quantity of C_2AH_8, and alumina gel. Among recent studies about hydration reactions may be noted Rodger & Double (1984), Ménétrier-Sorrentino et al. (1986), Capmas and Ménétrier-Sorrentino (1989), Gu et al. (1994). Also Rayment et al. (1994) studied the hydration reaction of CAC/slag mixtures and Fu et al. (1996) discussed the effect of different calcium aluminate hydrates on ettringite formation.

The hexagonal hydrate CAH_{10} is of particular interest in connection with conversion, because this hydrate is unstable both at normal and at higher temperatures and becomes transformed into cubic crystals C_3AH_6 and alumina gel. The compounds C_5A_3 and $C_{12}A_7$ are believed to hydrate to C_2AH_8.

1.5.3 Cement Replacement Materials

1.5.3.1 General

The hydration of cements become additionally complex when supplementary cementing materials such as Pulverised Fuel Ash (PFA), silica fume (SF) and blast-furnace slag (GGBS) are added. Blended cements have been of considerable interest, both scientific and technological, because of the advantageous effects of such additions: increase of chemical resistance to sulphate attack, impermeability, lowering of hydration heat and thermal expansion, easier workability and reduction in production costs.

This section discusses the chemistry and hydration reactions of PFA, SF and GGBS when blended in a general sense with Portland cement.

1.5.3.2 Hydration of Pulverised Fuel Ash and Pulverised Fuel Ash/Ordinary Portland Cement Systems

Pulverised fuel ash (PFA) or fly ash, is a pozzolanic material produced as a by-product from coal burning power stations and is used as cement replacement material. PFA consists of the fine ash particles (< 75μm), and is highly glassy, although the chemistry and phase composition of the ash is governed by coal quality and combustion conditions (Gumtz et al., 1986). Many ashes are dominantly aluminosilicates (in ASTM Class F ashes) while others may contain much calcium (ASTM Class C). The Class F fly ashes are characterised by their relatively high glass content, which also contributes to their reactivity with alkali and calcium hydroxides. The Class C ashes often contain substantially less glass of a higher Ca content, and a different suite of minerals, some of which are reactive, such as C_3A, C_2S, CaO (C), C_4AF, C_4A_3S and other sulphates (Roy, 1989). Table 1.8 gives the phase composition of UK PFAs.

Table 1.8: Bulk composition for typical UK PFA (Dhir, 1986)

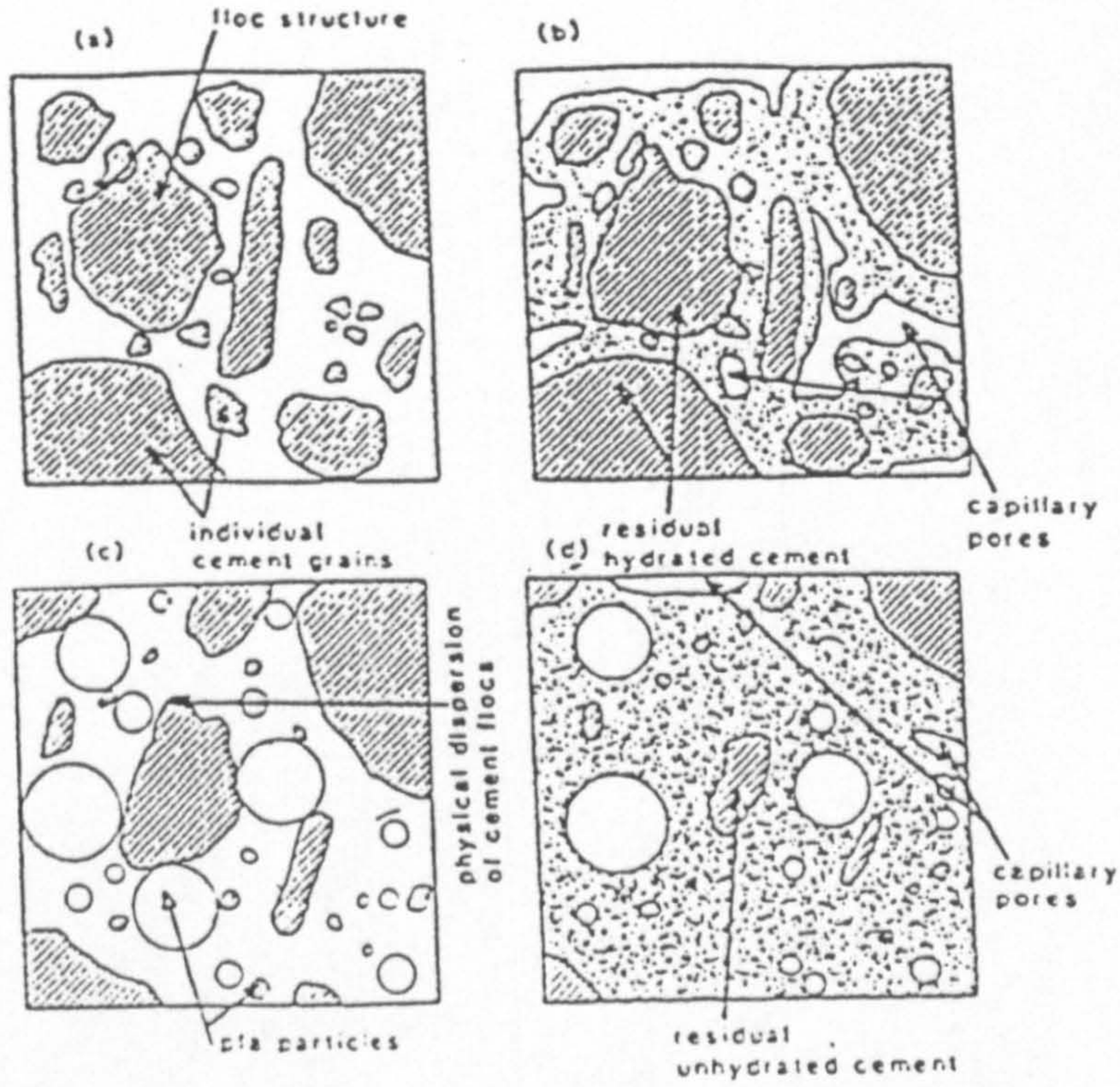
Oxide	OPC	Low Lime	High Lime
SiO_2	20	50	40
Al_2O_3	5	28	18
Fe_2O_3	3	9	8
CaO	64	3	20
MgO	2	1	4
SO_3	2	1	2
Others	4	8	8

The solution chemistry of the PFA /water systems is different from that of OPC. When water is first added to the anhydrous PFA, the more acid layer dissolves first and the water becomes temporarily slightly acid. The alkaline core then reacts with the other material in solution, the water becoming alkaline (Poon, 1985). Low lime PFA will not hydrate in the presence of water despite the dissolution of some components such as alkalis or calcium sulphates (Jensen, 1987). High lime PFA, however, will be involved in a number of reactions that are dependent on factors which do not only include ash chemistry. The presence of additional lime will promote pozzolanic reaction which can produce, for example, C-S-H, hydrogarnet and, when in the presence of gypsum,

ettringite. The mechanisms operating are well reviewed by Pollard et al., (1991) and a similarity with the hydration products of OPC is evident.

The effects of PFA on the hydration of cement pastes are complex. It is difficult to generalise about reactions in PFA bearing systems because of the variations between different PFAs and between different particles within a PFA.

Uchikawa (1986) reviewed the hydration chemistry of PFA and other composite cements. It has been suggested that the products of solution coming from the PFA will affect the initial hydration reactions of OPC. One of the possible reasons which may workers (Pratt, 1982; Grutzeck et al., 1985; Uchikawa, 1986) have suggested may be responsible for the retardation of the alite hydration is that the aluminate ions, released into solution by PFA, will deplete the calcium ion concentration by reacting with it. This would mean that not enough calcium ion concentration is present to react with the clinker minerals. Grutzeck also suggested that because the calcium ions were depleted by the PFA, this would result in delayed nucleation of the calcium hydroxide and the calcium silicate hydrate (C-S-H). Hydration of C_3A and C_4AF are affected similarly by retardation at early ages (Fagun et al., 1985) by clinker grains being coated with a protective layer of C_4AH_{13} and PFA-produced hydrates (Jensen, 1987). As the availability of sulphate and lime increases, ettringite is precipitated on the surfaces of PFA particles and the reactivity of C_3A increases as a consequence. Uchikawa et al. (1986) propose that the production of ettringite can be used to gauge the hydration rate of the interstitial phase. This suggests that the addition of PFA accelerates the hydration of the aluminate (C_3A) and ferrite (C_4AF) phases in cement after 1 day. Figure 1.4 shows a systematic representation of an OPC/PFA matrix.



Idealised model of the effect of PFA in freshly mixed concrete and the consequent hydrated microstructure. (a) Freshly mixed OPC concrete; (b) hydrated microstructure after 28 days; (c) the same concrete as (a) with PFA addition; (d) denser, more uniform hydrate microstructure after 28 days.

Figure 1.4: Systematic representation of an OPC/PFA matrix (Dhir, 1986)

1.5.3.3 Hydration of Silica Fume

Silica fume or microsilica (SF) is a by-product of the ferrosilicon and silicon metal industry. It is a highly reactive pozzolanic material with spherical particles, typically around 100nm in diameter, and consist largely of glass. Table 1.9 gives the chemical composition of the microsilica (Taylor, 1990). Silica fume addition influences the physical and mechanical properties of fresh and hardened concrete. Significant increases occur in the compressive strength and the impermeability of the cement paste.

Table 1.9: Chemical composition of microsilica from the production of elementary silicon and 75% ferrosilicon alloy

	Si %	75% Fe-Si
SiO_2	94-98	86-90
Al_2O_3	0.1-0.4	0.2-0.6
Fe_2O_3	0.02-0.15	0.3-1.0
MgO	0.3-0.9	1.3-3.5
CaO	0.08-0.3	0.2-0.6
K_2O	0.2-0.7	1.5-3.5
Na_2O	0.1-0.4	0.8-1.8
C	0.2-1.3	0.8-2.3
S	0.1-0.3	0.2-0.4
Loss	0.8-1.5	2.0-4.0

The ultra-fine particle size of SF (0.01 to 1 μm) when properly dispersed fill the interstices of the fresh cement paste structure, where they are available to react with the alkali hydroxide $Ca(OH)_2$ liberated by the hydrating Portland cement, forming insoluble C-S-H. This reaction is essentially similar to that of PFA, but at a much higher rate due to the vastly increased surface area of SF.

When used in proportions to replace up to 10% of cement, it significantly reduces bleeding and segregation of the mixtures. Some workers have shown that silica used as an addition with cement has considerable pozzolanic activity, which is detectable within hours and also that the early reaction of the alite is accelerated (Cheng-Yi & Feldmann, 1985; Halse et al., 1984; Babu et al., 1995; Saad et al., 1996).

C-S-H having a C/S ratio of about 1 has been reported to form at 20°C in 24 hours after mixing with water and at 38°C in only 6 hours (Grutzeck et al. 1982). The reaction of SF with $Ca(OH)_2$ is affected by the specific surface area, and the surface energy. When C/S ratio is less than 0.8, it is considered to be thermodynamically unstable. This lower C/S ratio tends to be confirmed in a report by Taylor (1986). Diamond (1982), Roy (1986) and Glasser (1987) have described the changing composition of pore solutions with longer time periods, which reflect the hydration processes occuring beyond the early ages.

Li et al. (1985) showed that while much SF is reacted in a SF-OPC mixture at 7 days, considerable unreacted SF remains. The early heat of hydration of SF-containing mixtures is frequently equivalent to that of high-early-strength cement, although the rate at which heat is liberated depends upon the proportions and the w/c ratio. Figure 1.5 gives the heat evolution calorimeter curves of cement with different proportions of SF (Cheng-Yi et al., 1985).

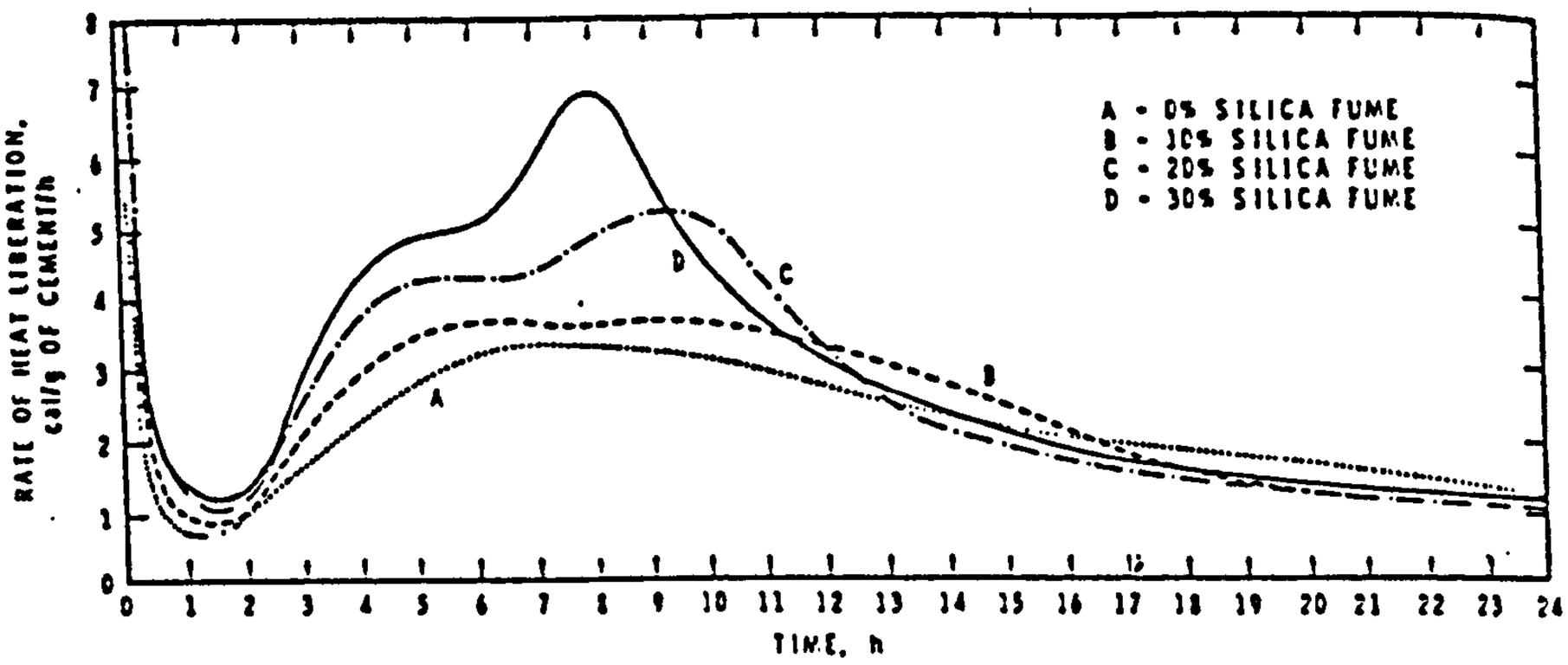


Figure 1.5: Change in rate evolution of cement-silica fume pastes with time (after Cheng-yi et al., 1985)

Roberts (1989) drew the following model of the physical and chemical processes which occur in Portland cement pastes containing SF and that summarises the discussion above:

1. The initial reaction rate of alite is increased, due to the slower formation of a lime-rich semipermeable membrane around the alite, related to rapid nucleation of CH or C-S-H on the silica surrounding the alite. Eventually a membrane leading to a normal induction period does build up unless the silica content is extremely high. During this time, higher than normal free $Ca(OH)_2$ contents can be reached, due to the more rapid alite hydration.

2. At the end of the induction period, hydration is accelerated by nucleation of C-S-H on the SF particles, or $Ca(OH)_2$ particles grown on the SF. The greater reaction degree and refinement of the hydration products provides the

increase in early compressive strength, frequently found despite little or no pozzolanic reaction.

3. At later ages, varying from several hours to several days, pozzolanic reactions begin to consume significant quantities of $Ca(OH)_2$, forming more C-S-H of lower C/S ratio, high degree of polymerisation, and lower density. These reaction products further refine the pore structure, thus increasing impermeability and strength.

From the above model it is evident that the early nucleation behaviour is critically important in providing large numbers of reaction product growth sites, which control the resulting microstructural changes.

1.5.3.4 Hydration of Blast Furnace Slag

Blast furnace slag is a by-product of the manufacture of iron, and is formed when iron ore is converted to iron. The slag in the air is then slowly cooled to produce a crystalline, dense material known as "air-cooled slag", or rapidly discharged and treated with water jets to produce a lightweight material known as "foamed slag" or the material is cooled quickly using water, as it comes out of the blast furnace, and is known as granulated slag. This quenching prevents the molecules from organising themselves into crystals and the slag will be in a glassy or vitrified state (Sersale, 1983).

The slag consists primarily of compounds formed by the reaction of SiO_2 and Al_2O_3 from the iron ore with CaO and MgO from the flux stone.

Slag cement is an uniform blend of granulated slag and hydraulic lime. Several types of cements are made using granulated slag, in amounts varying from 5% to over 90%. The hydration products of the Portland blast furnace slag cement are calcium tri-sulphoaluminate (ettringite), tobermorite, such as C-S-H phase, C_4AH_x or its solid solution or intergrowth with $C_3(A, F).CaSO_4.12H_2O$ and a small amount of $Ca(OH)_2$ (Ramachandran et al., 1981).

The hydration of slag cement is composed of two reactions: a Portland reaction and a slag reaction. The slag is activated by the lime made available during the hydration of the Portland cement fraction. Slag is more sensitive to heat than Portland cement clinker, because its apparent activation energy for hydration is higher (Roy et al., 1982). Granulated blast furnace slags normally are not hydraulic at room temperature. They require "activation" to initiate hydration and the availability of a mechanism for continuing the hydration process and normally, an alkaline activator is used. Shi and Day (1995) used a conduction calorimeter to monitor hydration kinetics of activated slag and found that the pH of the activator solution has an important role in the early formation of hydration products. Those hydration products are studied in more detail by Wang and Scrivener (1995) and Shi and Day (1996). The potential hydraulic activity of such slags is controlled first by thermodynamic considerations. The glassy phase which constitutes the bulk of properly granulated blast furnace slag is thermodynamically metastable with respect to an assemblage of crystalline phases having the same total composition (Wu et al., 1983).

The controlling factors of the slag hydration process apparently include (Roy et al., 1982):

1. the chemical composition (primarily of the glassy phase),
2. the glass structure,
3. the availability of active sites in the glass: chemical and physical defects (including those produced by fine combination),
4. availability of a reactive hydration or transport medium, such as a highly alkaline environment produced either artificially or by reaction of water with intermixed Portland cement,
5. presence of additional components which may generate low-free-energy-state reaction products,
6. effects consequent upon temperature elevation,
7. miscellaneous controlling factors such as water-cement ratio.

De Schutter & Taerwe (1995) described a new general hydration model, valid both for Portland cement and blast furnace slag cement. This hydration model enables the

calculation of the heat production rate as a function of the actual temperature and the degree of hydration.

Slag cements commonly give higher ultimate strengths than ordinary Portland cements at later ages and when the slag is finely ground, the strength development is equal to that of Portland cements at 3 days.

Development of a dense microstructure, a fine pore structure, and lower capillary porosity generates materials with lowered permeability and ionic diffusity, giving rise to generally superior chemical durability, including resistance to alkali-aggregate reaction.

1.5.4 The Waste/Cement System

1.5.4.1 General

When the solidification process is viewed as a waste/cement/water system, with the cement acting as a binder, the bulk chemistry is generally unlike that of concrete.

Solidified systems have a high degree of complexity due to the variability of wastes themselves. There is also the limited knowledge of the subsequent properties of the waste forms created, which are determined by both chemical and physical interactions of cement and waste. Here, some of the physical and chemical factors affecting solidification will be dealt in detail.

1.5.4.2 Physical Factors Affecting Solidification

The following physical characteristics of the waste can affect the setting time, curing time, strength, and other physical and chemical properties of the final waste form. They are:

* Particle size and shape
* Free water content
* Solids content
* Specific gravity/density

* Viscosity
* Temperature and humidity

Particle characteristics (size, shape, etc.) of a waste are one of the most important properties to solidification treatment. These characteristics can affect physical and chemical aspects of solidification reactions, and the properties of the solid product. Particle attributes, along with solids content, both suspended and dissolved, often determine whether a fast or slow setting process is to be used. Also, particle size can influence the diffusion of soluble, hazardous constituents from the interior of large particles into the interparticle space after solidification processing has been completed (Conner, 1990).

The problem with free water content is that the "free" water is chemically unbound and can react anywhere in the system. In other words, too much water may result in a layer of free-standing water on the surface of the solidified product, as well as reduction in strength and increase in permeability of the final product.

The solids content can affect both the setting and curing process, and the physical properties of the end product due to, first, the solids, including the solidification agents that may settle out and leave a two-phase system that is generally undesirable, and second, the final product may be weak mechanically, and thus unsatisfactory for the disposal scenario.

Related to specific gravity/density is the factor that large differences between the waste and the reagent result in a tendency toward phase separation. Although reagent particle size is generally small, it is not usually sufficient to make up for this difference, and some settling will occur unless viscosity is sufficient to prevent phase separation until the initial setting reaction can physically immobilise all components in place.

Also the solidification reactions speeded up with temperature, with some limitations. The humidity in the curing area must be kept high if the product is to cure properly. Evaporation of water from the surface will inhibit or stop solidification, and perhaps some fixation reactions in the surface layer.

1.5.4.3 Chemical Factors Affecting Solidification

It is understood the importance of retarding, inhibiting and accelerating the setting and curing of solidification systems. Many of the compounds, materials, and factors which are known to have such effects are listed in Table 1.10 (Conner, 1993). The effects are many and varied and are not simple to predict from knowledge of the composition of the waste. Often, a number of species are present, sometimes with opposing effects. The influence of the same species may also be dependent on concentration. Some studies have shown that some species can affect the degree of hydration through acceleration or retardation (Poon et al., 1985; Cartledge et al., 1990; Hills et al., 1992; Roy et al., 1992; Akhter et al., 1993; Hills et al., 1994a; Trussell et al., 1994).

Some of the general effects are interesting. For instance, ion exchange can inhibit or retard solidification system reactions by removing calcium from solution, and consequently preventing the ion in entering into the necessary cementitious reactions. It can also accelerate the process by removing interfering metal ions from solution. Which occurs may depend on the selectivity of the ion exchange material (Conner, 1993).

Metal Fixation Mechanisms and Methods

The mechanisms of fixation are different for the three primary groups of pollutants: metals, other inorganics, and organics. This work will confine itself to the fixation or immobilisation of metals.

However, before examining the mechanisms of fixation, there are general principles and practices that are common to many or all metals. They are:

1) Solubility of Metals

The solubilities of various metal species in pure water (aqueous solubility) are reviewed in the literature (Conner, 1990). However, differences between simple systems and real ones are illustrated by comparing values for individual species with those obtained in leaching tests on treated wastes (Conner, 1993). Nevertheless, as a starting point in choosing possible chemical reactions for fixation purposes, it is useful to know the basic water/acid/base solubilities of various species. The comparison also serves to point out the limitations of fixation technology in real applications or, in some cases, to show how

Table 1.10: Factors affecting solidification (Conner, 1990)

Compound or Factor	Effect	Mechanism Affected
fine particulates	I,P	P
ion exchange materials	I, A	I
metal lattice substitution	I, A	I
gelling agents	R, I, P-	P, I, M
organics,general	I, P, R	I, D
acids, acid chlorides	P-	I
alcohols, glycols	R, P-	I, W
carbonyls	R	I, D
chlorinated hydrocarbons	P-, R	I, M
grease	I, P	P
lignins	I	C
oil	I, P	P
starches	I	C
sulfonates	R	D
sugars	I, R	C
tannins	I	C
organics, specific		
ethylene glycol	P	I
hexachlorobenzene	P-, P+	I
phenol	P-	I
trichloroethylene	P-	I
inorganics, general		
acids	P-	I
bases	P-	I
borates	R	M
chlorides	R, P	I
chromium compounds (*)	A	I
heavy metal salts (*)	P-, A, R	I
iron compounds (*)	A	F, M
lead compounds (*)	R	M
magnesium compounds	R	M
salts, general	P-, A, R	I
silicas	R	F
sodium compounds	I	I
sulfates	R, P	I
tin compounds	R	M
inorganics, specific		
calcium chloride	A, R	M
copper nitrate (*)	P+	I
gypsum, hydrate	R	I
gypsum, hemi-hydrate	A	I
lead nitrate (*)	P-, P+	I
sodium hydroxide	P+, P-	I
sodium sulphate	P+, P-	I
zinc nitrate (*)	P+, P-	I

Note: **I**= setting/curing inhibition (long-term). **A**= setting/curing acceleration. **R**= setting/curing retardation (short term). **P+**= alteration of properties of cured product, positive effect. **P-**= alteration of properties of cured product, negative effect. **P**= coats particles. **I**= interferes with reaction. **C**= complexing agent. **M**= disrupts matrix. **F**= flocculent. **D**= dispersant. **W**= wetting agent. (*) Particularly relevant to this study.

the complex interactions of several mechanisms can achieve results better than those expected from simple theories.

In consideration of the above, it is important to understand that such comparisons assume a certain speciation for the metal, which in most cases has not been confirmed. Simplistic models of waste systems based on a single speciation of a metal in a waste may be invalid.

2) Metal Speciation in Wastes

It is desirable to know the speciation of the metals in the raw waste. However, complex waste systems, complete analysis is very difficult, time consuming and expensive.

Most wastes treated are not solutions, but are sludges, filter cakes, and other residues from waste water treatment systems. Unless complexed in soluble, stable form, a metal can usually be precipitated from solution as a species that exhibits minimum solubility under the expected disposal conditions. For instance: the metals have been precipitated with lime or other alkali, or with other agents, such as sulphide, to produce metal hydroxides, sulphides, or other compounds that have low solubility under the conditions of precipitation, usually in the pH range of 6 to 8 and a dilute water medium (Conner, 1990). This is especially important for the heavy metals of environmental interest which exhibit amphoterism, such as arsenic, cadmium, chromium, lead and zinc.

The hydroxides of these metals exhibit minimum solubility through a narrow pH range, usually in the area of pH 7.5 to 10, with solubility increasing rapidly as pH increases or decreases on both end of the range. Wastes whose metals are in solution have an important advantage from the fixation standpoint. The metal can be precipitated as the species of choice: silicate, sulphide, carbonate, etc. The solubility of the species produced will depend to some extent on other species present in solution, but the system can be optimised in any case. There are two major factors that place limits on the ability of a cement-based system to immobilise dissolved metals: *valence and complexation.*

Bishop (1988) , attributed the immobilisation of Cd, Cr and Pb in cement-based waste forms, even after all the alkali had been leached out, to chemical complexes formed

during such interactions with siliceous cement matrix. Other work has shown the same sort of immobilisation for metals, such as mercury, that do not form low solubility hydroxides, but it is believed to be as mercuric oxide (HgO) its final chemical state (McWhinney et al., 1990). Bhatty (1986) using pure tricalcium silicate (Alite, C_3S) instead of Portland cement, studied solutions of Cr, Cd, Pb, Hg, Zn so dilute that cemented solids were not formed. He speculates that four mechanisms may be involved in the fixation of metals by C_3S.

1. Addition: C-S-H + M → M-C-S-H
2. Substitution: C-S-H + M → M-C-S-H + Ca
3. Formation of New Compounds
4. Multiple Mechanisms

The major factors for immobilisation of waste forms, or containment mechanisms include:

- pH control
- Redox potential control
- Chemical reaction
  * hydroxide precipitation
  * carbonate precipitation
  * sulphide precipitation
  * silicate precipitation
  * ion-specific precipitation
  * complexation
- Adsorption
- Chemisorption
- Passivation
- Ion exchange
- Diadochy
- Reprecipitation
- Encapsulation
  * microencapsulation

* macroencapsulation

* embeddment

- Alteration of waste properties

Some of these mechanisms were already discussed by some authors (Poon, 1985; Cartledge et al., 1990; Conner, 1990; Cocke, 1990; Roy et al., 1992; Wiles et al., 1992; Lin et al., 1993; Macphee et al., 1993; Kindness et al., 1994) and are discussed below.

pH Control

It is widely accepted that cement and pozzolan based waste forms rely heavily on pH control for metal containment.

Normally, high pH is desirable because metal hydroxide have minimum solubility in the range of pH 7.5 to 11. However, some metals, as previously mentioned, exhibit amphoteric behaviour.

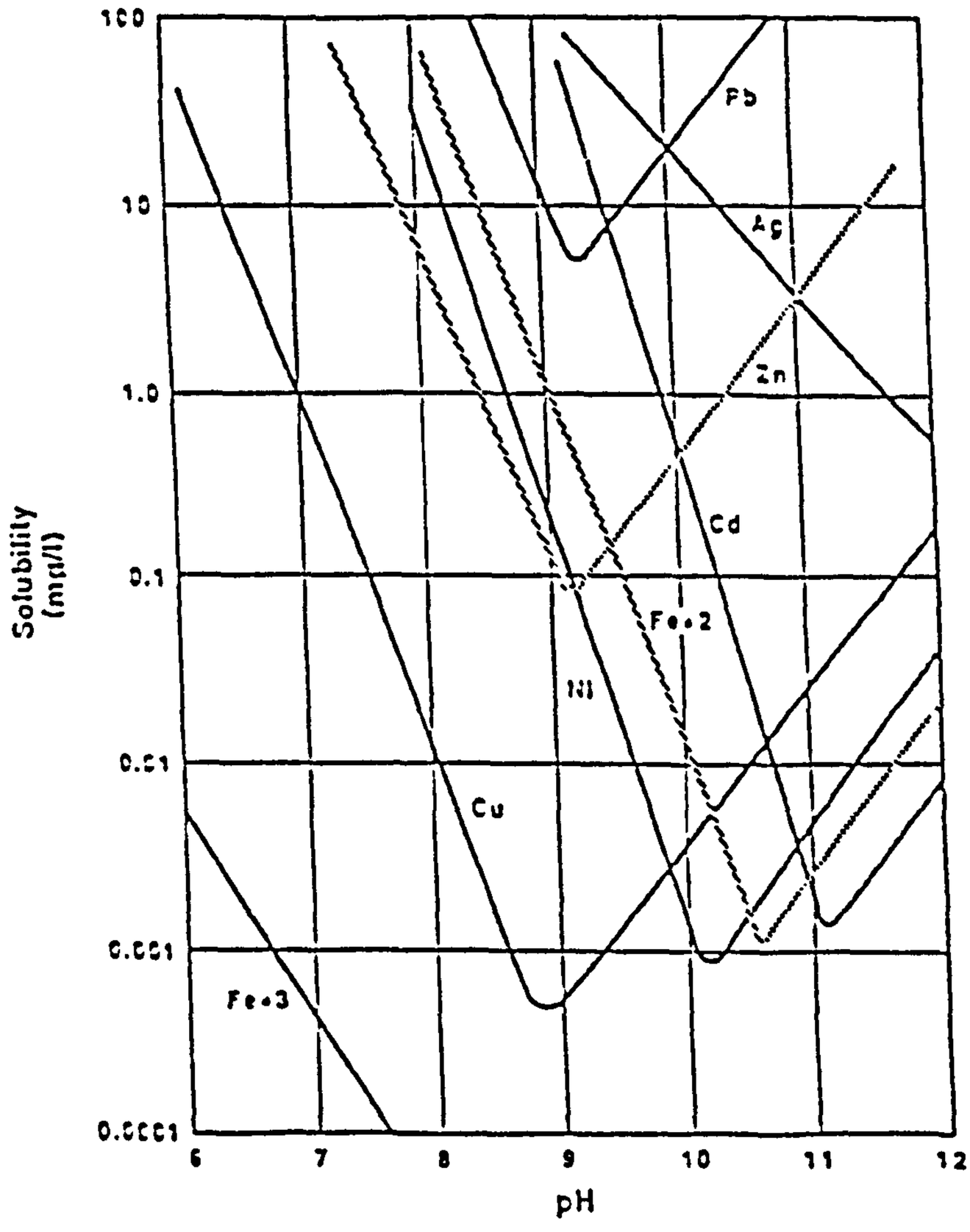


Figure 1.6: Solubilities of metal hydroxides as a function of pH (Conner, 1990)

Unfortunately, all metals do not reach minimum solubility at the same pH, so that the optimum pH of the system must be a compromise (Conner, 1993). This is illustrated by the solubility curves for various metal hydroxides in water as shown in Figure 1.6.

Redox Potential

The redox potential, Eh, is the oxidation - reduction potential (ORP) referred to the hydrogen scale, expressed in millivolts. It establishes the ratio of oxidants and reductants existing within the waste-environment system, and may affect the valence state of a metal in that system.

Relatively little attention has been paid to this factor by workers in the field. It is an area which needs more elucidation. Chromium is one example of the influence of valence state on solubility. Arsenic is another. The presence of strong oxidants or reductants can change the valence state of a number of the metals, affecting their chemical speciation and, therefore, their mobilities by orders of magnitude (Jula, 1974).

Chemical Reactions

By far the most important fixation mechanism for metals in cement-based systems is chemical precipitation as low solubility species. Metals can be precipitated as hydroxides, carbonates, sulphides, silicates, ion-specific and complexation.

a) Hydroxide Precipitation:

Hydroxide precipitation occurs when the pH of a solution of dissolved metal ions is raised to some optimum level for a specific metal. The optimum pH is different for each metal and, often, for different valence states of a single metal.

b) Sulphide Precipitation:

Most metal sulphides are less soluble than the hydroxides at alkaline pH (arsenic is an exception), as illustrated in Table 1.11.

However, metal sulphides can resolubilize in an oxidising environment, and there is currently disagreement over the acceptability of metal sulphide sludges in uncontrolled landfills (Moore et al., 1988) .

Table 1.11: Comparison of hydroxide and sulphide solubilities (Conner, 1993)

	Approximate Solubility (mg/l)		
Metal	**Hydroxide**	**Sulphide**	**Difference Factor**
Iron	5×10^{1}	1×10^{-4}	5×10^{3}
Cadmium	3×10^{0}	1×10^{8}	3×10^{8}
Chromium	1×10^{-3}	None	None
Copper	2×10^{-2}	2×10^{13}	1×10^{11}
Lead	2×10	6×10^{-9}	3×10^{8}
Mercury	6×10^{-4}	1×10^{21}	6×10^{17}
Nickel	7×10^{-1}	6×10^{-8}	1×10^{7}
Silver	2×10	4×10^{-12}	5×10^{12}
Zinc	3×10^{2}	1×10^{-6}	3×10^{8}

Note: Difference factor = Hydroxide solubility/sulphide solubility

c) Silicate Precipitation:

The reactions of polyvalent metal salts in solution with soluble silicates have been studied extensively over many years. The best known process uses a combination of Portland cement and sodium silicate. The reactions of soluble silicates in solution is best summarised by Vail (1952) who states:" *The precipitates formed by the reaction of the salts of heavy metals with alkaline silicates in dilute solution are not the result of the neat stoichiometric reactions describing the formation of crystalline silicates, but are the product of an interplay of forces which yield hydrous mixtures of varying composition and water content."*

These reaction products are usually non crystalline and therefore very difficult to characterise structurally.

d) Carbonate Precipitation:

In certain cases, metal carbonates are less soluble than their corresponding hydroxides (Conner, 1993). In cement chemistry, the natural formation of carbonates from carbon dioxide from the air is termed "carbonation". McWhinney et al. (1993), Bonen et al. (1994) have already shown an increase in surface carbonate formation in all metal-ion doped cement.

The carbonate species, CO_3, dominates at pH values larger than 10.3. The carbonation process at alkaline pH takes place according to:

$$Me(OH)_2 + H_2CO_3 \rightarrow MeCO_3 + 2H_2O \quad \text{(Eq. 1.3)}$$

Inorganic Complexation

Some complexes can produce insoluble metal species that may have lower solubilities than the simple metal compounds. This approach to fixation in cement-based field has not been deliberately used commercially.

Adsorption

In a solid, molecules are held together by a variety of types and magnitudes of cohesive forces. At solid surfaces, cohesive forces are unbalanced, giving rise to the phenomenon of adsorption.

Three major sorptive ingredients which can be used in S/S are activated carbon, clays and exchanged clays.

Chemisorption

Retention of one chemical species by another by close range chemical or physical forces is known as chemisorption. The binding forces are greater than those of pure adsorption but do not represent a true chemical bond. There is no sharp boundary of distinction between adsorption and chemisorption but functionally the major difference is that chemisorbed species do not desorb easily.

Passivation

Passivation is another phenomenon important in S/S treatment. Metal ions dissolving from a solid surface may precipitate on the surface after contacting an anion in solution which forms a less soluble species. If the precipitate forms a tight, impermeable layer, it may block or inhibit further reaction at the surface.

Ion Exchange

The deliberate addition of ion exchange materials to solidification formulations has had limited use, but common reagents often have limited ion exchange properties i.e. clays, soils, cements and fly ashes.

Diodochy

When one element substitutes for another of similar size and charge in a crystal lattice, this is known as diodochy. An example of this is zinc or magnesium for calcium in Calcite. Bishop (1988) postulates that chromium and lead are bound into a silica matrix in Portland cement waste forms, possibly as silicates. Replacement of silicon is questionable but coexistence as hydrated metal oxides is a possibility.

In order to improve and extend solidification process, research is being carried out by a number of workers to elucidate the mechanisms involved in the fixation of waste species, as already cited. In particular, some waste materials solidified commercially are known to be capable of deleterious interferences with commonly used binding agents. Examination of these materials, for example by Jones (1988), Peer (1993) and Hills et al. (1994), has shown that normal hydraulic and pozzolanic reactions may be significantly retarded or poisoned. Although some of these materials appeared to "set" and harden in the laboratory, there is mounting evidence to suggest that for some wastes this is a consequence of the effects of exposure to atmospheric CO_2. The next section will focus on a review of work that has been developed in the field of carbonation of solidified waste, which is the basis of this work.

1.6 REVIEW OF PREVIOUS WORK IN CARBONATION OF CEMENT-BASED MATERIALS

1.6.1 General

Carbonate cementitious systems are not new. Man has used alkaline earth hydroxide cements and mortars which harden due to their reaction with the CO_2 in the atmosphere for thousands of years (Bukowski et al., 1979).

In recent years it has become increasingly clear that there can be significant differences between cover and uncovered cementitious systems related to its CO_2 absorption (Parrott, 1992). A recent example of the ability of cements to carbonate was registered among the people who spent 2 years sealed inside Biosphere 2, and began to run short

of breath. Scientists were puzzled that within the Biosphere they could not find the CO_2 that the supposed organisms should have been producing. Later on, they found that concrete inside the structure absorbed a massive amount of CO_2 (Hecht, 1994). Fresh concrete contains about 30% calcium hydroxide, which slowly combines with CO_2 to form calcium carbonate and water. Inside the biosphere, where CO_2 levels were high, the reaction proceeded very quickly.

If carbonation is prone to take place in waste forms, as already shown by some researchers (McWhinney et al., 1993 and Conner, 1993), then, can carbonation have an influence on the stabilisation and fixation of the solidification process?

The interest in the effects of carbonation on heavy metals solidification systems has increased in the scientific community, however, the influence of CO_2 on the hydration process with respect to the solidification of metal pollutants has not yet received any attention (Mollah et al., 1993).

The scope of the following review includes a description of the carbonation phenomenon, and a brief literature review of carbonation applied to blended and non-blended cement pastes. The main carbonation reactions with the cement hydrates are discussed, with the factors that influence the rate of carbonation. The importance of accelerated carbonation, followed by a summary of the state of the art applied to solidification of hazardous wastes is also given.

1.6.2 Carbonation

Carbonation of material is the chemical process denoting the reaction of calcium hydroxide with carbon dioxide resulting in the formation of calcium carbonate and water.

Carbon dioxide dissolves in the pore solution of cement paste, producing CO_3^{2-}, which reacts with Ca^{2+} to produce $CaCO_3$. The OH^- and Ca^{2+} ions required by these reactions are obtained by the dissolution of CH and decomposition of the hydrated

silicate and aluminate phases. C_4AH_x is quickly converted into C_4ACH_{11} and ultimately into $CaCO_3$ and hydrous alumina; mono-sulphate and ettringite yield $CaCO_3$, hydrous alumina and gypsum. C-S-H is decalcified, initially by lowering of its Ca/Si ratio, and ultimately by conversion into a highly porous, hydrous form of silica (Verbeck, 1958; Suzuki et al., 1985; Taylor, 1990).

Carbonation is a natural phenomenon acting upon cement-based systems: the action of carbon dioxide in air (0.03% in air) (Curtil et al., 1993). Carbonation begins at exposed surfaces, and spreads inwards at a rate proportional to the square root of time (Taylor, 1990). In fact, from the thermodynamic viewpoint (equilibrium state at infinite time), all the hydrate or anhydrous compound with calcium must undergo carbonation.

1.6.2.1 Carbonation of Portland and Calcium Aluminate Cements

The published literature on carbonation and its effects on cement paste is extensive. Parrott (1987), reviewed thoroughly carbonation in reinforced concrete. Others, such as Roy (1986), reviewed carbonation and transport. Hansson (1984), Turriziani (1986), Dhir et al. (1992) and Parrott (1994) corrosion related to carbonation. Suzuki et al. (1985), Kobayashi et al. (1994) studied the mechanism of carbonation of C-S-H in suspensions. Barret et al. (1983) discussed equilibria relevant to the stabilisation of silicate structures by carbonation. Young et al. (1974), Naik (1979) and Young et al. (1992) studied the effects of carbon dioxide on development of strength of cement paste. Carbonation of calcium aluminate cement was thoroughly studied by Blekinsop et al. (1985a,b).

The work initiated by Mollah et al. (1992a, 1992b), related to the effects of carbon dioxide on cement-based solidification processes will be discussed in more detail in section 1.6.7.

1.6.2.2 Carbonation of Mineral Admixtures

The literature is also rich in papers dealing with carbonation of blended cements. Some important papers were produced by Buttler et al. (1983), Thomas et al. (1992) and Malami et al. (1994), studying the effect of carbonation in concrete containing

pulverised fuel ash. Osborne (1986), Bier et al. (1989), and De Ceuckelaire et al. (1993) have studied carbonation of blast furnace slag concretes; while Skjolsvold (1989) and Byfors (1989) carbonation applied to concrete with silica fume.

1.6.2.3 Chemical Background on Carbonation Reactions

The reactions involving the CH and C-S-H may be represented by the following equations (Taylor, 1990):

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \qquad \text{(Eq. 1.4)}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad \text{(Eq. 1.5)}$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad \text{(Eq. 1.6)}$$

$$xCaO.SiO_{2(aq)} + zH_2O \rightarrow yCa^{2+} + zyOH^- + (x\text{-}y)CaO.SiO_{2(aq)} \qquad \text{(Eq. 1.7)}$$

C-S-H (calcium silicate hydrate) and calcium hydroxide are the principal binding agents of hydrated cement. Calcium sulfoaluminates may also occur, typically in the form of slender needlelike crystals. They are also subject to reactions with carbon dioxide but are a relatively minor constituent of cement paste (Mindess & Young, 1981).

C-S-H appears to decompose into calcium carbonate by a pseudomorphic reaction that results in no change in morphology, whereas calcium hydroxide is believed to first dissolve into the water phase where it reacts with dissolved CO_2 and precipitates as $CaCO_3$. The calcium carbonate that forms as a result of carbonation reactions is typically in the form of calcite, aragonite, or more rarely as vaterite. The proportions of the type of carbonates have been shown to depend on the degree of hydration. The silica product shown in reaction is in the form of a pure gel.

1.6.2.4 Factors Affecting the Rate of Carbonation

The rate of carbonation of cementitious materials is affected by the cement type, porosity, permeability and water/cement ratio. The partial pressure of carbon dioxide also plays an important role. Kamimura et al. (1965) and Venuat and Alexandre (1968) found that relative humidity exerts a strong influence on the rate of carbonation. They showed that the rate was maximised at a relative humidity near 50% and decreased markedly as the humidity was changed from this value. Carbonation has also a close relation with the chemical composition of pore solution in concrete. If the pores are filled with water, the penetration of CO_2 is hindered because of the low rate of diffusion of CO_2 in water, while if the pores are completely dry the reaction of CO_2 with water molecules is absent (Saetta et al., 1993). Compacted specimens must be used where the space between the cement particles are only partially filled with water. Even then, carbonation in the interior is slow and incomplete as the outside layers are carbonated. This is partially due to pore blockage and partly due to the very high rate of evolution of heat which evaporates the remaining water (Young, 1992).

There is disagreement in the literature as to whether calcium hydroxide or C-S-H in cement material is more susceptible to carbonation. Venuat and Alexandre (1968) and Calleja (1980) both conclude that calcium hydroxide is the more reactive component whereas Slegers and Rouxhet (1976) suggest that C-S-H is the more reactive phase, pointing to such evidence as the presence of unreacted calcium hydroxide in carbonated samples in which the C-S-H phase had been fully carbonated. Richardson and Groves (1993) demonstrated through a model for C-S-H gel that it could successfully link experimentally derived data on silicate anion structure and Ca:Si ratio for the C-S-H present in hardened C_3S pastes both before and after carbonation and this model has been extended to incorporate elements other than Ca, Si, O and H. The model is based on a highly disordered layer structure comprising finite silicate chains in a "solid solution" with a variable amount of $Ca(OH)_2$. This model can have some direct utilisation in solidification technique applied to heavy metals.

1.6.2.5 The Effects of Carbonation on Cement Paste or Binder

The main consequence of carbonation is the drop of the pH of the pore solution of concrete from between 12.5 and 13.5, to a value of about 8.3 in fully carbonated paste, (Saetta et al., 1993) so that the passive layer that usually covers and protects the reinforcing steel against corrosion becomes no longer stable.

Apart from the effect on reinforcement corrosion, carbonation has both good and bad effects on cement-based systems. It markedly increases the compressive and tensile strengths of Portland cement mortars and concretes, sometimes by as much as 100%, in the regions affected (Young et al., 1974). Figure 1.7 (Young et al., 1974) shows a comparison of compressive strength development in carbonated and normal hydrated mortar compacts. Strength development in C_3S was very rapid, compared to that which occurs with normal hydration, and the behaviour of β-C_2S during carbonation is very similar to that of C_3S when the initial sluggish period (within the first 9 min.) is neglected. The dynamic system resulted in slower strength development initially but improved development at the longer ageing times. This behaviour could result from either starvation of CO_2 or water in the later stages of reaction or microcracking caused by the higher thermal stresses, which most likely develops during the very rapid early stage reaction in the static system. This condition occurred even in those specimens exposed to prolonged carbonation. The strengths also increase if the binder is a composite cement made with 40% of slag (Taylor, 1990). Carbonation also makes a specific and substantial contribution to irreversible shrinkage; as Lea (1970) pointed out, this indicates that the C-S-H is attacked. It may cause superficial crazing, and can contribute significantly to the drying shrinkage measurements on small specimens. The reduction in permeability due to carbonation of the surface layers results in a decrease in the reversible volume changes with subsequent variations in relative humidity.

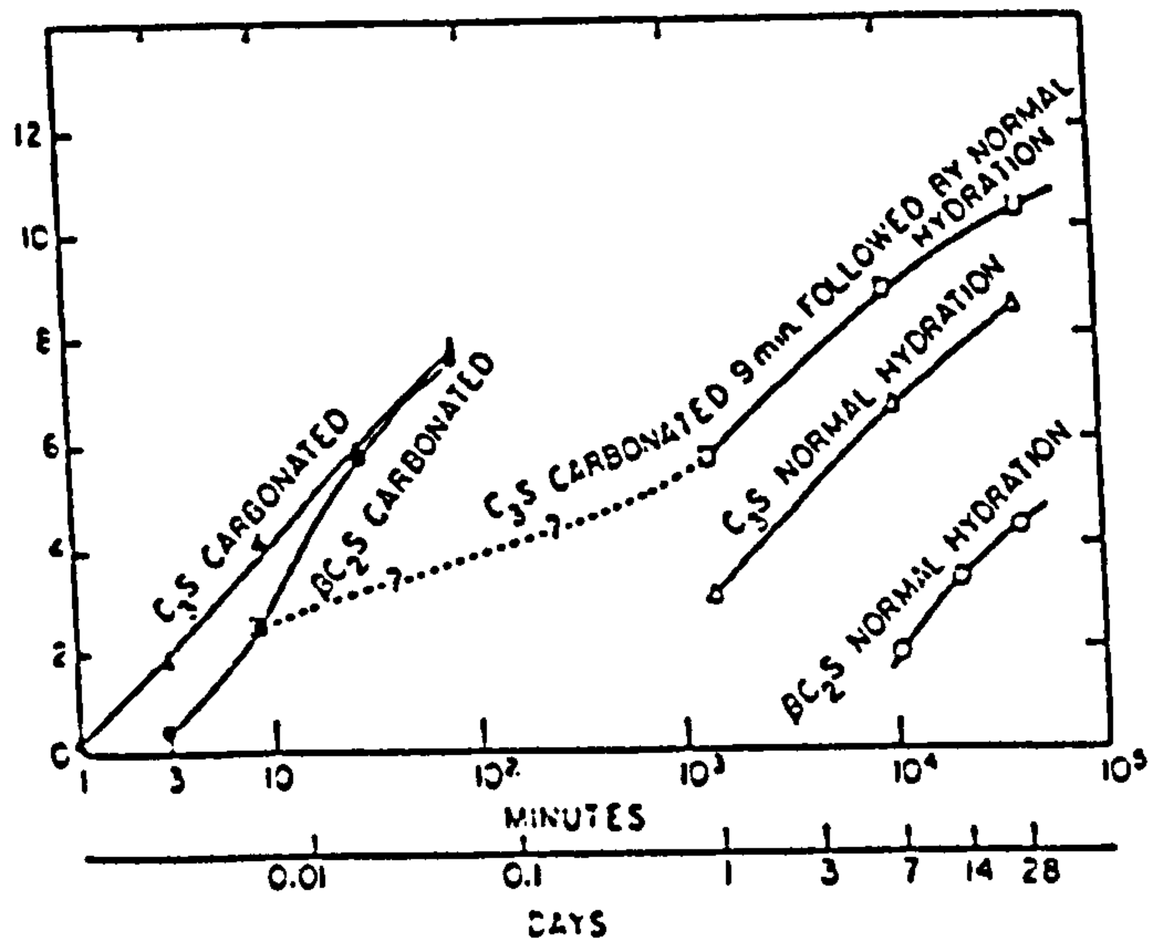


Figure 1.7: Comparison of compressive strength development in carbonated and hydrated mortar compacts (after Young et al., 1974)

1.6.2.6 Laboratory Based Accelerated Carbonation

Commercial interest in the ultra-rapid hardening of fresh Portland cement paste by treatment with gaseous carbon dioxide can be traced back to the mid-19th century (Maries, 1992). The chemistry of such accelerated carbonation was first studied nearly as long ago as 1896 (Passow, 1896), but was not investigated in any detail until quite recently (Berger, 1972; Sorochkin et al., 1975; Malinowski et al., 1983; De Ceukelaire et al., 1993).

The kinetics of accelerated carbonation have now been studied and the sequential mechanism has been postulated for the complete process of carbonation (Maries, 1992). They are:

1. Diffusion of CO_2 in air. Mixing air with CO_2 decelerates carbonation very considerably.
2. Permeation of CO_2 through concrete.
3. Solvation of $CO_{2(g)}$ to $CO_{2(aq)}$
4. Hydration of $CO_{2(aq)}$ to H_2CO_3. This is a slow and usually rate-determining step. The solvation and hydration of CO_2 are important in biological

respiration and in chemical manufacturing processes, and have therefore been extensively studied.

5. Ionisation of H_2CO_3 to H^+, HCO_3^-, CO_3^{2-}. This takes place almost instantaneously, lowering the pH locally by 3 or more units.
6. Dissolution of cement phases. Because the process is cyclic, this step is both rapid and extensive. About 25% of the cement reacts within a few minutes, generating an appreciable exotherm.
7. Nucleation of $CaCO_3$, C-S-H.
8. Precipitation of solid phases. Depending on humidity and temperature, either vaterite or aragonite may form initially, but these metastable polymorphs of calcium carbonate eventually revert to calcite. Moreover, not all the $CaCO_3$ appears as crystalline material.
9. Secondary carbonation. C-S-H gel forms as the result of normal hydration, and may then be progressively decalcified, converting ultimately to " S-H " and $CaCO_3$.

Accelerated carbonation is strongly exothermic, and immediate temperature rises of 20°C are commonly observed in the concrete. Hardening is extremely rapid, and compressive strengths of several MPa can be atteined within minutes. Nevertheless, after the supply of CO_2 has been stopped, the cement continues to hydrate more or less as usual into a normal, durable paste exhibiting high dimensional stability. Sorochkin et al. (1975), have shown also that carbon dioxide diffusion into cement paste is more rapid at low water/cement ratios.

Furthermore, carbon dioxide is able to activate cementitious compounds which would otherwise be considered too poorly hydraulic for practical use, such as γ-C_2S and calcareous wastes. This, together with elevated early strength, high hydration exotherm and stabilised shrinkage properties, offers opportunities for novel cementing systems and process applications.

1.6.2.7 Carbonation of Cement-Based Solidified Waste

The influence of carbon dioxide on the hydration process with respect to the cement-based solidification of metal pollutants has not yet received much attention.

In the last 15 years the majority of the research has concerned the effect of carbonation on porosity, strength, permeability, hydration of CaO, C-S-H, etc. as mentioned before. However, since 1990, some investigators have examined the role of carbonation on the hydration reactions of metal doped Portland cement-based materials and an understanding of the nature of hydration reactions in the presence of carbon dioxide and in its absence has improved.

McWhinney et al. (1990a,b), have studied the solidification of metal ion pollutants (Ba, Cr, Pb, Zn, Cd and Hg) in cement and noted that high carbonation has a feature common to all doped cements. However, the extent of carbonate formation is greater for the zinc, cadmium and mercury-doped cements. The mechanism of hydration for mercury-doped cement is different from other metals as microscopic inclusions of mercury can be identified.

Mollah et al. (1992a) have investigated the effects of carbonation on cadmium solidified waste. Evidence from a FTIR (Fourier Transform Infrared Spectroscopy) investigation showed that the hydration of OPC was retarded due to the formation of calcium hydroxycadmiates, which resulted from the surface reaction of $[Cd(OH)_4]^{2-}$ with calcium ions at or on the surface of the cement grains. In the same work, carbonation was found to play an important role in the hydration and polymerisation of the silicates phases.

The same authors have also evaluated the effects of CO_2 on chromium and zinc-doped S/S systems (1992b, 1993). The characterisation of chromium-doped OPC before and after leaching was examined using FTIR, EDS (Energy Dispersive X-Ray Spectroscopy) and SEM (Scanning Electron Microscopy). Both atmospheric carbon dioxide and the dopant were found to have significant effects on the chemical state of the silicates. The authors showed that both CSH and CH are competing for atmospheric

CO_2 and again that the silicate regions hold much of the information about the mutual interactions of the dopant metals and the silicate complexity present in OPC.

Smith and Walton (1991) have demonstrated that precipitation of calcite due to carbonation of cement paste can affect the mass transport of radionuclides that have been previously solidified, and they may coprecipitate with the calcite forming solid solutions.

Bonen and Sarkar (1995) have found that carbon dioxide can have a profound effect on the leaching characteristics of heavy metals and the microstructure of the cement binder, by forming a layered structure composed of a leached zone, calcium carbonate-rich layer, and a unleached core, which may stabilise metal carbonate precipitates.

The works cited above show that the effect of carbonation on the polymerisation of the orthosilicate units present in OPC and the formation of calcite have an important influence on solidification of metal pollutants thereon is an important area of research and might have beneficial implications on solidification technology. Although the work with doped cement paste is an important addition to the literature, work involving real waste materials has not been carried out. This is an important omission from cement research effort because it has been shown that the synergistic effects of compounds, which on there own may be compatible with OPC, may cause deleterious waste/binder interference effects. Furthermore, the research that has been carried out frequently used OPC, and the importance of selecting appropriate binders other than OPC to immobilise waste compounds has to be taken into account in order to maximise the effective solidification and fixation of the waste material within the carbonated waste form.

1.7 SUMMARY

Hazardous waste management in the EC has been in a continuous state of transition for over a decade as a succession of directives has sought to rationalise and unify a wide range of policies.

In the UK, the Environmental Protection Act of 1990 is still by far the most important environmental law, which requires industries to have manufacturing processes audited by environmental agencies and are subject to the "Duty of Care" principle.

Nevertheless, waste minimisation is not widely carried out and a continuous effort is being made by some sectors to increase its importance. Most of the waste produced in the UK is sent to landfill for disposal without treatment. More recently, the draft EC Landfill Directive and Landfill Tax Regulation are encouraging many industries to submit their waste to a pre-treatment in order to make it less harmful to the environment.

Solidification processes are designed to improve the physical and chemical characteristics of hazardous wastes before disposal. Cement-based solidification is often the technology of choice for immobilising soils and sludges containing a variety of pollutants. Different types of cement, blended and non-blended, can be applied during the process, with OPC being the most common one. However, the presence of the toxic and potentially deleterious chemical compounds may be available to adversely affect the cementing matrix.

Carbonation is a common feature for Portland cement-based materials, and some workers have observed that solidified waste forms are also susceptible to this phenomenon. Examination of the literature shows that there is little published work regarding the effects of carbonation on cement-solidified waste forms. It is important, therefore, to improve the quality of solidified wastes, not only because unstable solidified materials are a potential threat to the environment, but also because of the commercial and economic aspects associated with increasing waste management legislation. Carbonation appears to have an important influence on the properties of cementitious systems and its effects on cement solidified waste requires investigation.

1.8 OUTLINE OF THE PRESENT WORK

Chapter 2 describes the materials and experimental methods used to examine the mechanical, microstructural and chemical properties of the solidified waste forms.

Chapter 3 is devoted to a preliminary investigation into the effects of carbonation on a commercial industrial waste solidified with OPC. The samples are cured under three different environments and then tested for mechanical, microstructural and chemical properties.

Chapter 4 explores the effects of carbonation on the mature properties of two blended inorganic industrial wastes bound to different blended binders. The current understanding of hydration of Portland and calcium aluminate cements as well as the carbonation phenomenon on these cementitious materials are discussed.

Chapter 5 studies the kinetic of carbonation reaction at atmospheric pressure and at room temperature. The degree of carbonation for each cement system is determined. The process governing the diffusion of carbon dioxide into waste forms is discussed with reference to the variation of water/cement and waste/binder ratios for the different systems studied.

Chapter 6 examines the physico-chemical properties of mix designs that exhibited different degrees of carbonation, as shown in Chapter 5, and a comparison between these samples is discussed.

Chapter 7 studies the effects of carbonation on cements doped with single laboratory grade metals. The microstructural, mechanical and chemical properties are described and the mechanisms by which heavy metals are incorporated into the carbonated system are elucidated.

Chapter 8 gives a general discussion, pointing the original contributions and suggestions for further work. Chapter 9 concludes the Thesis.

1.9 OBJECTIVES OF THE PRESENT WORK

The main objectives of this work are:

i) To investigate the effects of natural and accelerated carbonation on the development of mechanical and microstructural properties of solidified products and the fixation of metallic waste components, using real wastes and laboratory grade materials.

ii) To elucidate the fixation of metals in carbonated waste forms.

iii) To examine the influence of different binders on the properties of carbonated solidified waste forms.

iv) To study the kinetics of accelerated carbonation reaction in the presence of different waste/binder materials

CHAPTER 2

MATERIALS AND EXPERIMENTAL METHODS

2.1 PREVIEW

In Chapter 1 a general introduction to waste management was presented. Legislation and practices employed in the UK and Europe were reviewed with, an emphasis to solidification technology. A review of the current understanding of cement-based solidification, focusing on the main cementitious binders and their applicability in waste/cement systems as well as the physical and chemical factors affecting solidification was presented. Then, a detailed review of carbonation of cement-based materials, described the main carbonation reactions with cement hydrates and solidified hazardous wastes. In that Chapter the scope of the Thesis was defined: the study of the effects of carbonation on the development of mechanical, microstructural and chemical properties of solidified waste products.

The aim of this Chapter is to describe the materials, and experimental methods used throughout this work. It is important to be aware of the many different tests that can be applied to measure the performance of solidified waste forms. Some of these tests are mandated by state or local regulators and others are employed to provide additional assurance that a given solidification process is appropriate.

The materials and experimental methods described in this work are divided in three and four sub-groups, respectively:

<u>Materials</u>

1. Portland and calcium aluminate cements
2. Cement replacement materials (PFA, SF and GGBS)
3. Industrial wastes

Experimental Techniques

1. Physical tests
2. Leaching tests
3. Microcharacterisation
4. Measurement of the consumption of CO_2 - 'Eudiometer' test

and they will be discussed in the following sections.

2.2 MATERIALS

A range of binders were selected to cover as wide a range of chemical and mineralogical compositions as possible, within the most commonly used cementitious systems. These binders were used to treat two commercially solidified industrial wastes, predominantly composed of heavy metals. The suppliers and chemical analysis of these materials are described below.

2.2.1 Portland and Calcium Aluminate Cements

Table 2.1 gives the suppliers, Bogue and oxide analysis of the different types of cement used in this work. The chemical analysis were given by the suppliers. The cements were kept in sealable plastic bags in a covered plastic container at laboratory controlled conditions.

2.2..2 Cement Replacement Materials

The properties and suppliers of the three admixtures used in this work are shown in Table 2.2. The chemical analysis were given by the suppliers.

2.2.3 Hazardous Wastes

Two industrial wastes that are commercially solidified in the UK were used in this work in an attempt to explore the effects of carbonation on real wastes.

They are predominantly heavy metal wastes and the samples were obtained direct from the source. These materials were kept sealed in plastic containers. The same batch of both wastes were use throughout the work. Table 2.3 gives the suppliers of the waste, date of collection, solid contents and type of process.

Table 2.1: Analysis of cements used (%w/w)

Cements	OPC	RHPC	WOPC	SRPC	CAC
Supplier	Blue Circle	Blue Circle	Blue Circle	Blue Circle	Lafarge
Phase					
C_3S	52	54	64	57	-
C_2S	19	18	22	19	-
C_3A	7	9	4.4	0	-
C_4AF	6	8	1.1	17	-
CA	-	-	-	-	-
$C_{12}A_7$	-	-	-	-	-
C_2A_5	-	-	-	-	-
Oxide					
SiO_2	20.4	20.5	24.5	21.4	4.9
Al_2O_3	4.1	5.1	1.9	3.6	51.6
Fe_2O_3	2.1	2.7	0.35	5.7	1.5
CaO	63.8	64.1	68.7	64	37.2
Free Lime	1.5	1.0	2.5	0.6	na**
MgO	2.1	1.2	0.55	0.7	na
Alkali Eq.*	0.6	0.7	0.2	0.5	na
SO_3	2.9	3.3	2.0	2.0	na
IR* **	0.4	-	< 0.1	0.6	na
LOI* **	3.2	1.2	1.0	1.5	na

* Alkali Equivalent = $Na_2O + 0.658\ K_2O$; ** na = not available; ***IR = Insoluble Residue %

LOI = Loss on Ignition %

Obs.: Aluminate phases were not determined, however, CA, $C_{12}A_7$ and C_2A_5 were known to be present but not quantified.

Table 2.2: Analysis for pozzolanic materials

Pozzolans	PFA	SF	GGBS
Supplier	Ready Mixed Concrete	Ready Mixed Concrete	Civil & Marine Ltd.
Oxide %			
SiO_2	47.7	89	33.2
Al_2O_3	25.7	1.5	14.3
Fe_2O_3	11.3	1.2	0.3
CaO	2.3	0.6	42.3
Free Lime	na	na	na
MgO	1.7	0.6	6.6
Alkali Eq.*	3.4	0.6	0.5
SO_3	1.2	na	na
TiO_2	1.0	0.2	0.6
P_2O_5	na	0.1	0.05
C	na	1.4	na
Mn_2O_3	na	0.3	na
S total %	na	na	0.8
Glass content %	na	na	99

* Alkali Equivalent = $Na_2O + 0.658\ K_2O$ na = not available

Table 2.3: Description of waste sludges used in this work

Waste	Date of Collection	Solid Contents	Type of Process	Suppliers
Cory Waste (W1)	Oct./93	55%	Commercially Solidified/Stabilised waste	Cory Waste Environment Ltd., West Turrock-Essex
Metal Colours (W2)	Oct./93	30%	Zn Plating	Metal Colours Waste, Slough

One waste known here as Cory waste was obtained from a solidification operation which used an OPC/PFA blend which is a derivative of the product Stablex. Here, the incoming wastes were pre-treated and converted to an alkaline slurry before solidification.

The chemical analysis of both wastes are given in Table 2.4. The anion content, total organic carbon, pH results were supplied by the two companies. The metal content of the wastes were determined in triplicate and analysed using a Philips PV 8050 Inductively Coupled Plasma Emission Spectrometer, (ICP-AES) after acid digestion in HNO_3 and HCl (Vogel, 1989). This technique is described in more detail in section 2.3.2.

Table 2.4: Chemical analysis of the industrial wastes

	W1 (Cory Waste)	W2 (Metal Colours Waste)
Metals (mg/Kg)		
Sr	215	175
Cr	6638	11275
Cu	8650	175
Mn	3137	1675
Ni	4825	312
Pb	3265	288
Sb	1201	25
Zn	19475	41%
Cd	1025	< 0.1
Ba	575	125
As	7464	200
Hg	2514	< 0.1
Anions (mg/L)		
Cl^-	419	24.7
SO_4^{-2}	1112	725
NO_3^-	648	2362
Total organic carbon (mg/L)	2.0	1.1
pH	8.0	8.4

Wastes were received in the form of filter cakes and oven dried at 105°C to constant weight. Then, the material was ground using a pestle and mortar to a particle size of less than 500 μm. This procedure was executed to enable a consistent product to be used during this study. Samples were stored in air-tight containers.

2.2.3.1 Preparation of the Samples

An adopted procedure for the preparation of the solidified waste forms was to mix the dry wastes with cement using a food mixer (blended or non-blended) at varied water/solid (w/s) ratios and cast in PVC moulds. Two different cylindrical moulds were used in this work: cylinders with 32 mm X 32 mm and with 50 mm X 50 mm. They were left to cure in atmosphere-controlled containers and allowed to mature for 28 days in the following environments: nitrogen, air (laboratory bench - ambient) and carbon dioxide. The temperature and humidity of the room were constantly monitored and were found to vary between 20°C ± 3 and 50% rh ± 8, respectively. The carbon dioxide environment was maintained at a 50% - 60% relative humidity by passing the gas through a wash bottle containing $Mg(NO_3)_2.6H_2O$ solution to condition the gas to a nominal 50% rh, which is reported to produce the maximum rate of carbonation in hydrated Portland cement (Young et al., 1974).

After 2 days samples were demoulded and returned immediately to their respective containers. At 28 days samples were physically, chemically and microstructurally examined and the following section describes these test procedures. For the measurement of carbon dioxide uptake a slightly different sample preparation procedure was carried out and this is described in section 2.3.4.

2.3 EXPERIMENTAL METHODS

The purpose of this section is to describe the experimental tests used in this work. They are divided in four groups for convenience with reference to the equipment, experimental procedures and calculation of results.

2.3.1 Physical Tests

Many existing physical and construction tests are applied for the testing of solidified waste forms. Such tests are important to establish material handling characteristics and differentiate among the attributes of different binders. In this work, unconfined compressive strength (UCS) was determined. Physical strength in cement solidified wastes develops over a period of several days. Thus, 28 days, which is commonly used in construction materials testing, was used as a standard time for comparison of strength development in this study.

2.3.1.1 Unconfined Compressive Strength

The UCS test measures the shear strength of a material without lateral confinement. It is a measure of the ability of a solidified product to resist mechanical stresses such as might be imposed in a landfill by overburden or heavy land-moving equipment (EPS report, 1991). The test is outlined in British Standards BS 4550 (1978).

Equipment

UCS was determined using an Instron 1195 compression testing apparatus, fitted with a 10 KN or 20 KN load cell, as appropriate, and with a crosshead speed of 1.0 mm/min.

Experimental Procedure and Calculation of Results

After 28 days, cylinders were subjected to a vertical force and the maximum force obtained prior to breakage of that cylinder was noted. Waste-free samples were also prepared and used to compare and assess the effect of the addition of the waste on the sample strength.

The cast faces of specimens were prepared by grinding, where necessary, prior to testing and the number of specimens broken for a single strength value was generally four. The results were given as a mean with estimated standard deviation* .

* In this work estimated standard deviation (ESD) was used to measure the variability of the data. ESD= range/4, and this is based on the empirical rule that states that approximately 95% of the measurements lie in the interval y±2s. The length of this interval is, therefore, 4s.

2.3.2 Leaching Tests

The performance of solidified wastes is generally measured in terms of leaching and extraction tests. Leaching tests measure the potential release of contaminants to the environment. A number of different leaching tests are available, and one or more may be required for regulatory approval. In this work the leaching test used was recommended by the draft on EC Landfill Directive (1993). The test was a modified DIN 38 414 leaching procedure, which accomodated a reduction in sample size and maintained the specified liquid to solid ratio.

In all tests, the waste is exposed to a leachant and the amount of contaminant in the leachate (or extract) is measured and compared to a previously established standard.

Equipment

In this recommended leaching test, two methods were used to analyse the leachate. A pH meter, to indicate the acid-to-base balance of the leachate; and a Inductively Coupled Plasma Emission Spectrometry (ICP-AES) for the analyses of leachate metal content.

The pH meter used was a Philips PW 9490 - Glass electrode.

The ICP-AES used was a Philips PV 8050. Figure 2.1 shows a schematic diagram of a typical ICP-AES system.

ICP is similar to atomic spectrometry. The main difference is that the flame used is of sufficient power to cause collision excitation and ionisation of a nebulised sample. Samples are introduced into the central channel of an Argon plasma at 8000 K as a finely dispersed mist, which is rapidly dissolved and vaporised. During transit through the plasma core dissociation and ionisation occurs. Ions are extracted from the central channel of the plasma through a vacuum pumped interface containing a cooled metal sampler cone, separated from the bulk of the Argon and transmitted into the detector. The intensity of light which is given off as these ions fall to lower energy states is measured at specific wavelengths and used to determine the concentration of the elements of interest (Skoog et al., 1992). One of the advantages of this technique is that

a large number of elements can be excited and their concentrations determined at one time.

Experimental Procedure and Calculation Results

Broken cylinders from the UCS test provided samples for leach testing using the DIN 38 414 leaching procedure. The leachant used in this test is deionised water with a liquid to solid ratio of 10:1. The samples were prepared in triplicate and turned end-over-end for 24 hours. The pH before and after a 24 hours extraction procedure was measured. The leachate was filtered through a Whatman GF/C paper and analysed by ICP-AES. The results were given as a mean with estimated standard deviation.

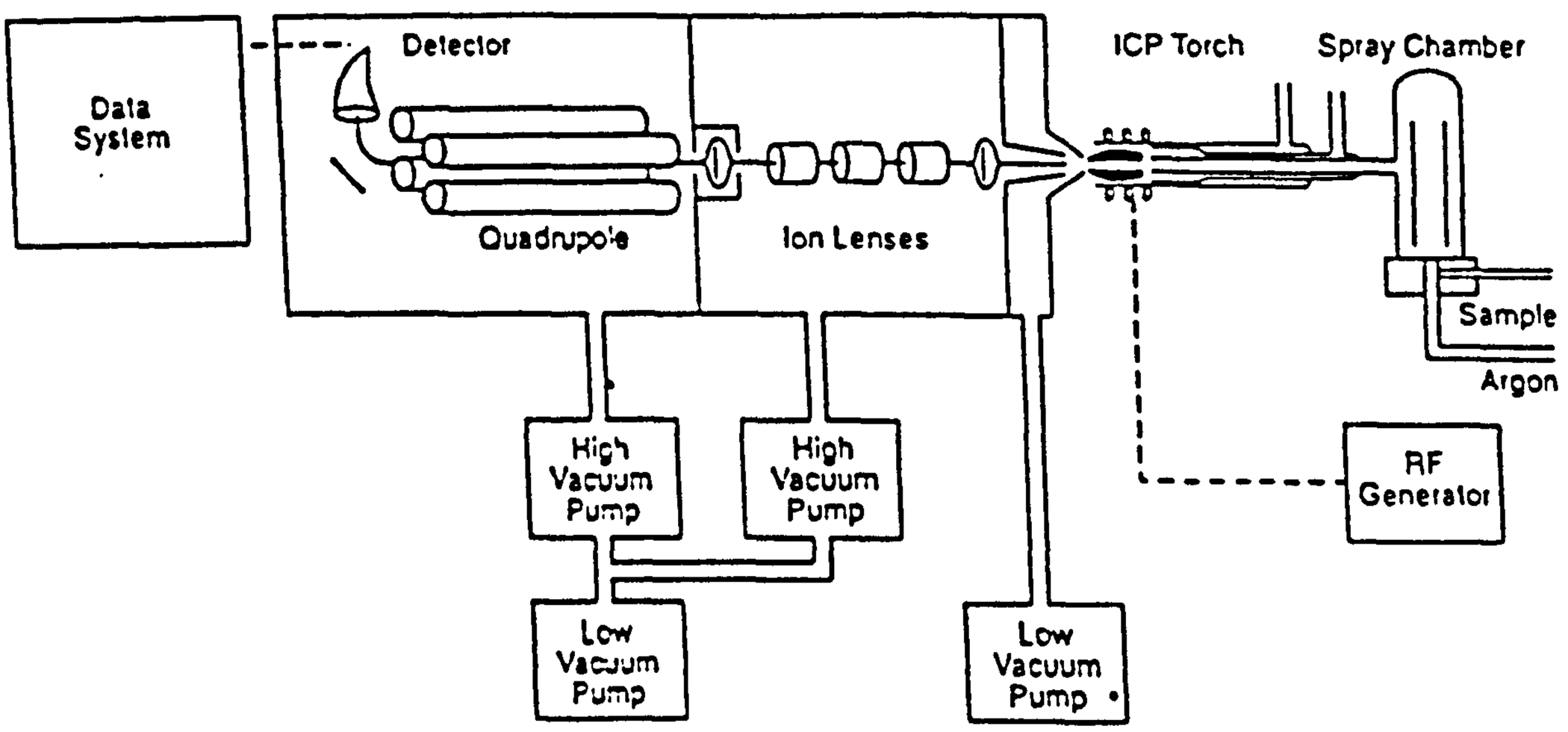


Figure 2.1: Schematic diagram of an ICP-AES system

Samples for analysis by ICP-AES are usually acid digested, for example as when the dry waste is analysed for metal content (section 2.2.3) or pH controlled by the addition of further acid such as the samples from the leaching test. This ensures that the atomised solution maintains a consistent droplet size (by minimising the differences in solution viscosity) and this reduces the possibility of sampling error from this source (Sager, 1992). The minimum detection limit for this equipment was < 0.1 mg/L.

2.3.3 Microcharacterisation Tests

Special techniques developed for mineralogical and materials science testing are used to characterise materials presented for solidification. These tests can be applied to elucidate the structure of waste forms and enable a better understanding of the physico-chemical form of the contaminants. In this work four tests were used as discussed below. They are: X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA), fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR)

2.3.3.1 X-Ray Diffraction

X-ray diffraction examines the crystal structure of a material. X-rays are scattered and diffracted by the lattice structure of crystals and this principle is used to provide a method of analysis. The condition for diffraction of an X-ray beam is given by the Bragg equation.

Bragg Equation: $n\lambda = 2d \sin\theta$

Where: n = order of diffraction (usually 1)

λ = wavelength of the radiation (in this case copper, 1.5404 Å)

θ = the angle of diffraction

When a X-ray beam strikes a crystal surface at some angle θ, a portion is scattered by the layer of atoms at the surface. The unscattered portion of the beam penetrates to the second layer of atoms where again a fraction is scattered, and the remainder passes on to the third layer. The cumulative effect of this scattering from the regularly spaced centers of the crystal is diffraction beam (Skoog et al., 1992). In other words, atoms located exactly on the crystal planes, which are arranged in a regular repetitive manner, contribute by constructive interference to a diffracted beam. Atoms located between the planes, however, contribute destructive interference and this results in a diffraction pattern characteristic of a particular crystal structure.

This technique has been used to study Portland cement since 1938 (Gutteridge, 1984). Many difficulties are found such as peak shifting and broadening with solid solution

which is frequent shown by crystalline phases and hydrated products that are often amorphous and do not produce sharp peaks.

During this work, X-ray diffractometry was used qualitatively to identify phases formed specifically when carbonation takes place and also to follow the hydration of wastes in general.

Equipment

Figure 2.2 shows an X-ray diffractometer system. The specimen is irradiated by a monochromatic, parallel beam of X-rays while being rotated about the diffractometer axis. Reflected X-rays are recorded by a counter which is traversing the same axis, but at twice the angular speed of the specimen, thus ensuring that the correct position is maintained. The signal from the counter is sent to a computer, which may be used to edit the signal received. In this study the diffractometer used was a Philips 2000 series diffractometer, using CuK-alpha radiation.

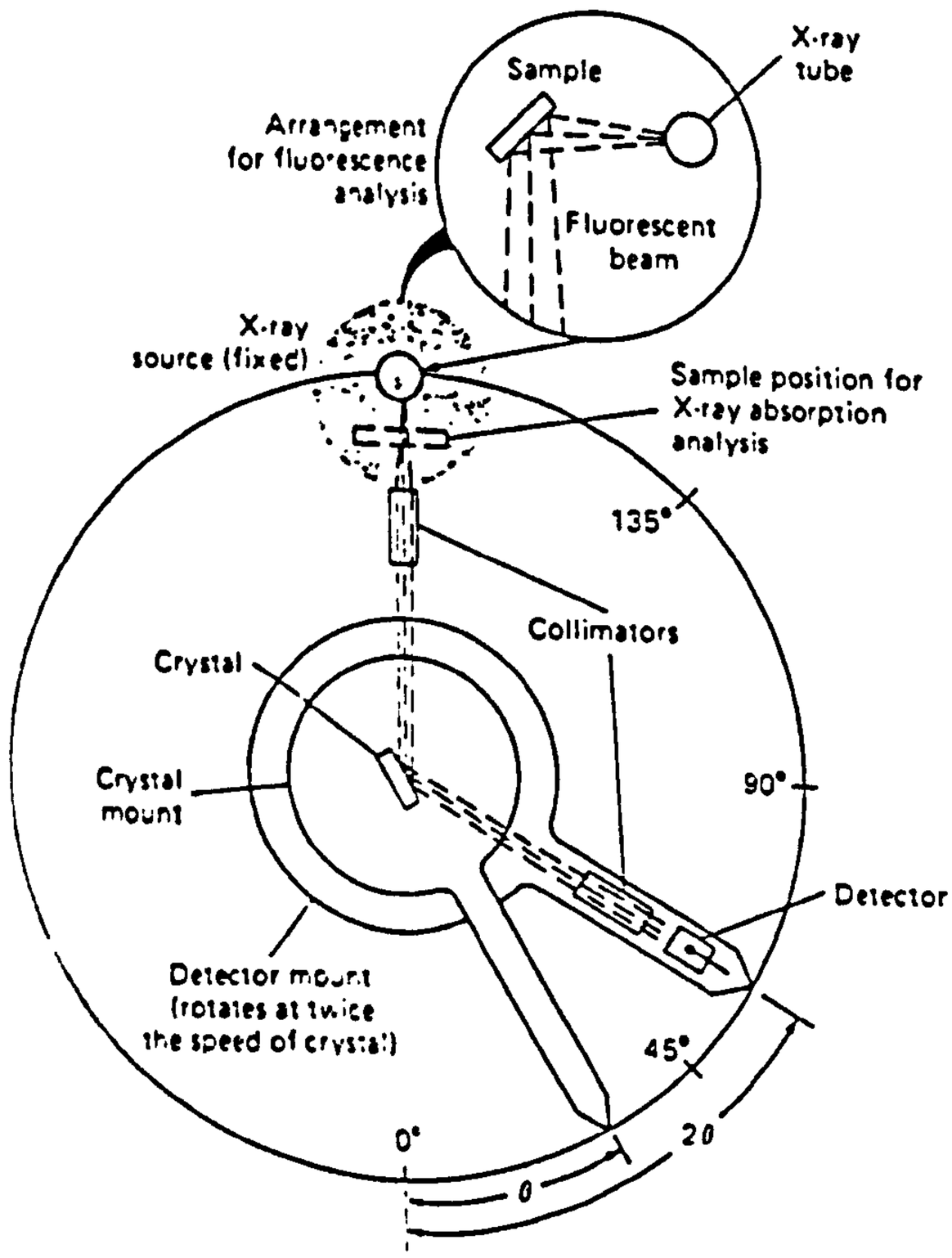


Figure 2.2: X-ray diffractometer - X-ray monochromator and detector

Experimental Procedure and Calculation of Results

The samples prepared as described before, were ground in an agate mortar and pestle to a fine homogeneous powder (<150 μm). The ground sample were kept in sealable plastic bags, which were de-aired. Samples were pressed by hand into the sample holder and placed in the diffractometer. The scanning angle chosen was 5.0 to 55.0 degrees 2-θ at a scanning rate of 1° per minute.

Analysis of the diffractograms was usually carried out using the ASTM powder file index of Portland cement and associated minerals.

2.3.3.2 Scanning Electron Microscopy

SEM is a technique used to examine the physical structure and chemical make up of the surface of a material on the microscopic scale. The method provides a large depth of field, so it is frequently possible to observe three-dimensional structures in a sample. By adding an EDXA detector to the SEM, it is possible to obtain simultaneous, multielement analysis. Therefore, this technique can be useful in determining the physico-chemical form of the contaminant in solidified waste forms.

This technique was first used on Portland cements in the 1960's. It is generally used to examine fracture or polished samples which have been previously dried.

Equipment

Figure 2.3 is a schematic diagram of a SEM. Energetic electrons are injected into the system and they are produced by a hot wire filament. This filament is maintained at a potential of 1 to 50 kV, although during this work a 10-20 kV accelerating voltage was used. Electrons pass through a small hole in the accelerating electrode and emerge as a narrow monochromatic beam, which enters the electromagnetic optical system of the microscope. The specimen is, therefore, bombarded by a finely focused beam of electrons which when incident produce low energy secondary electrons, that are detected as a layer near the specimen surface. The signal produced is displayed synchronously with the electron beam on a monitor. A high resolution image of even the fine structures on the surface of the specimen can be achieved and, as the intensity of

electrons is related to atomic number and orientation of surface features, these are generally shadowless and closely resemble stereographic optical images.

The specimens were examined in this study with a Hitachi S-450 fitted with a Link Analytical (AN-10000 microanalysis) system and a low vacuum JEOL 5410 LV SEM with ISIS EDX.

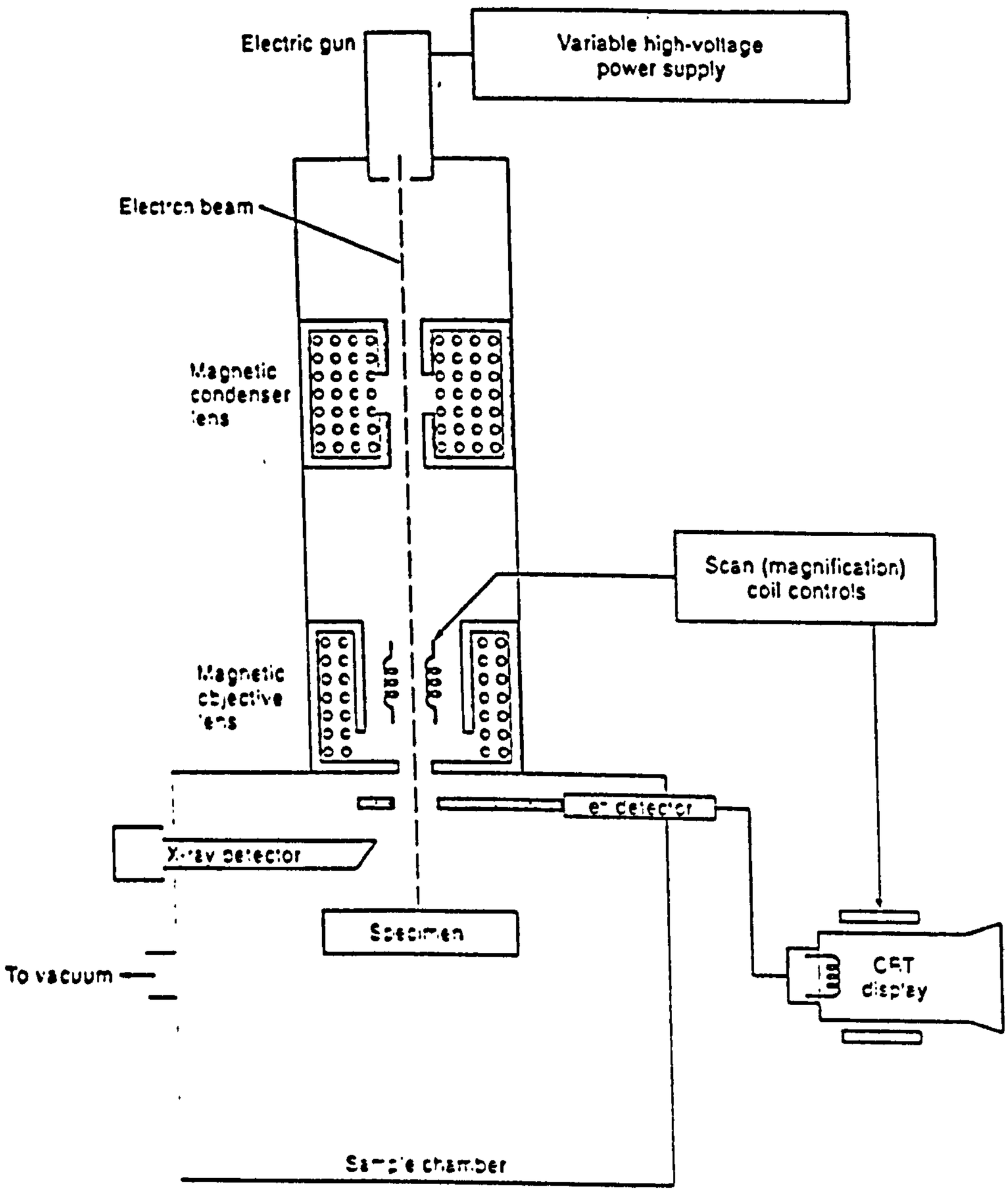


Figure 2.3: Schematic diagram of a SEM system

Experimental Procedure and Calculation of Results

Both fracture and polished specimens were used in this work. The fracture specimens were mounted on stubs and the polished sections were embedded in araldite and a epoxy polymer and polished using a diamond paste. As those materials are non-conductive, they require coating with either a carbon or gold film. Gold coating is more useful for high quality images , but does cause some interference when energy-dispersive analysis of X-rays is required, when the use of carbon is preferential despite a reduction in image resolution. The two techniques used to collect and examine the results are the energy dispersive X-ray analysis and backscattering electron imaging.

Energy Dispersive X-Rays Analysis (EDXA)

When electrons having several kilovolts energy strike a selected target on a solid specimen X-rays characteristic of the atoms present in the specimen are produced and with suitable detectors these X-rays can give a chemical analysis of the areas being viewed in the SEM, this technique is called EDXA. The target area is typically about 5 μm square and enables, where specimen geometry and target size allow, a semi-quantitative analysis to be obtained.

Back Scattered Electron Imaging (BEI)

Some of the electrons in the beam which strike the specimen undergo elastic scattering. That is a change of direction with little loss of velocity, due to collisions with the nuclei of atoms partly screened by the bound electrons. After one or more such collisions the electrons may re-emerge from the specimen. Such electrons are called backscattered electrons. These backscattered electrons are detected by a semiconductor device. Elastic scattering becomes more abundant as the atomic number of the material increases, so both the signal and the brightness of the image increase as we go up the periodic table. Consequently, the backscattered electron image is very useful in revealing differences in composition which can then be followed up by X-ray analysis. The phases of Portland cement are quite readily distinguished, for example, portlandite, one of the main hydration products will appear as mid-gray colour whereas anhydrous material is lighter and porosity is black.

It is important to mention that digital images were used together with the conventional photographic reproductions of the backscatter SEM micrographs. The digital images increase vastly the effectiveness and clarity of the visual information. A comparison between both visualizations has been made by Bonen (1996).

Also, all schemes for carrying out quantitative analysis of solid specimens use a standard of known composition. X-ray intensity ratio between the elements of interest in the specimen and the same element in the standard are measured. Both specimen and standard are examined in identical conditions. This gives the measured relative intensity ratio commonly called K. Once K values have been obtained they must be corrected for several effects. In particular: a) the atomic number factor Z; b) the absorption factor A; c) the fluorescence effect F. This is known as the ZAF technique (Goldstein et al., 1992). In this study semi-quantitative analysis was used.

2.3.3.3 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy can identify the presence or absence of functional groups in a molecule. The class or type of compound can be deduced, although positive identification of the exact composition is not always possible.

Absorbing (vibrating) groups in the infrared region absorb within a certain wavelength region, and the exact wavelength will be influenced by neighboring groups. The electronic transitions that take place are due to the absorption of radiation by specific types of groups, bonds, and functional groups within the molecule. The wavelength of absorption is a measure of energy required for the transition. Its intensity is dependent on the probability of the transition occurring when the electronic system and the radiation interact and on the polarity of the excited state. FTIR can indicate changes in the silicate, sulphate and carbonate phases when hazardous compounds are mixed with the cement paste, and that is particularly important in this study.

Equipment

A spectrometer is an instrument that will resolve polychromatic radiation into different wavelengths. All spectrometers require a source of continuous radiation over the wavelengths of interest, a monochromator for selecting a narrow band of wavelengths

from the source spectrum, a detector for converting radiant energy into electrical energy and a device to read out the response of the detector. Infrared radiation is essentially heat, and so hot wires, light bulbs are used as sources. The infrared region extends from about 0.78 μm to 300 μm, but the range from 2.5 to 15 μm is the most frequently used for analysis. The 0.8- to 2.5- μm range is also known as the near-infrared region. The monochromator consists of mirrors or lenses. The FTIR differs of conventional IR spectrometers exactly in this point, where rather than a grating monochromator, a FTIR instrument employs a interferometer to obtain a spectrum.

The FTIR process a number of advantages, such as a greater through-put, increased signal-to-noise ratio, simultaneous measurement of all wavelengths. Figure 2.4 gives a schematic illustration of an interferometer for FTIR spectrometry.

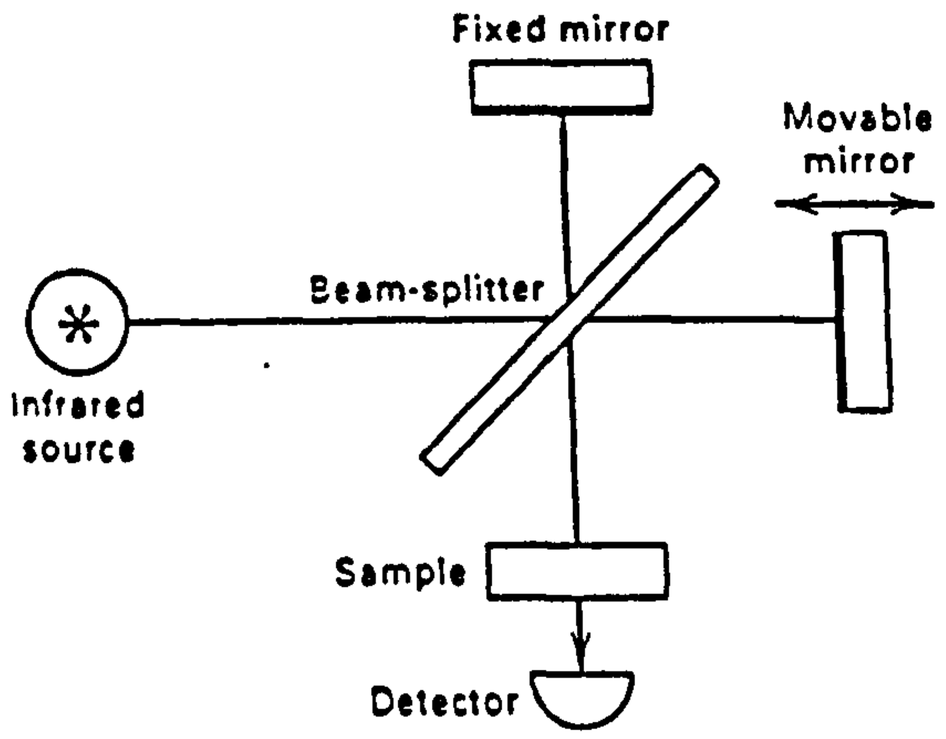


Figure 2.4: Schematic diagram for an interferometer for FTIR spectrometer

Radiation from a conventional IR source is split into two paths by a beam-splitter, one path going to a fixed position mirror, and the other to a moving mirror. When the beams are reflected, one is slightly displaced (out of phase) from the other since it travels a smaller (or greater) distance due to pattern (of all wavelengths in the beam) before passing through the sample. The sample sees all wavelengths simultaneously, and the interference pattern changes with time as the mirror is continuously scanned at a linear velocity. The result of absorption of the radiation by the sample is a spectrum in the time domain, called a *interferogram*, that is, absorption intensity as a function of the optical path difference between the two beams. This is converted, using a computer, into

the frequency domain via a mathematical operation known as *Fourier Transformation.* A conventional appearing infrared spectrum results.

In this work infrared spectra was recorded on a Perkin Elmer 1300 series spectrometer.

Experimental Procedure and Calculation of Results

Samples previously ground to a particle size < 150 μm were mixed with KBr (which is transparent in the infrared region) and pressed into a pellet for mounting for measurement. The spectrometer was run in the range of 4000 - 400 cm^{-1} at 32 scans/min. The spectrum obtained was qualitatively examined in order to identify different phases on the carbonated and non-carbonated solidified waste products.

2.3.3.4 Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy identifies and characterises molecules. Data from NMR analysis delineates complete sequences of groups or arrangements of atoms in a molecule. NMR has proved to be a powerful tool for analysing the Si and Al components of Portland cements and studying the details of their hydration characteristics (Macphee et al., 1988; Tong et al., 1990; Cong et al., 1993).

Nuclear magnetic resonance spectroscopy is based upon the measurement of absorption of electromagnetic radiation in the radio-frequency region of roughly 4 to 600 MHz. In contrast to infrared absorption, nuclei of atoms are involved in the absorption process. Furthermore, in order to cause nuclei to develop the energy states required for absorption to occur, it is necessary to place the analyte in an intense magnetic field.

Equipment

Figure 2.5 is a block diagram showing the NMR components. The central component of the instrument is a highly stable magnet in which the sample is placed. The sample is surrounded by a transmitter/receiver coil.

The excitation pulses are produced by a crystal-controlled continuous oscillator having an output frequency of ν. This signal passes into a pulser switch and power amplifier, which creates an intense and reproducible pulse of radio-frequency radiation, which

passes into the transmitter coil. The resulting free induction decay signal (FID) is picked up by the same coil (which now serves as a receiver), is amplified, and is transmitted to a detector. The phase-sensitive detector computes the difference between the nuclear signals and the crystal oscillator output, which leads to the low-frequency, time domain signal shown on the right of the Figure 2.5. This signal is digitised and collected in a computer for frequency analysis by a Fourier transform program. The output from this program is plotted giving a frequency domain spectrum.

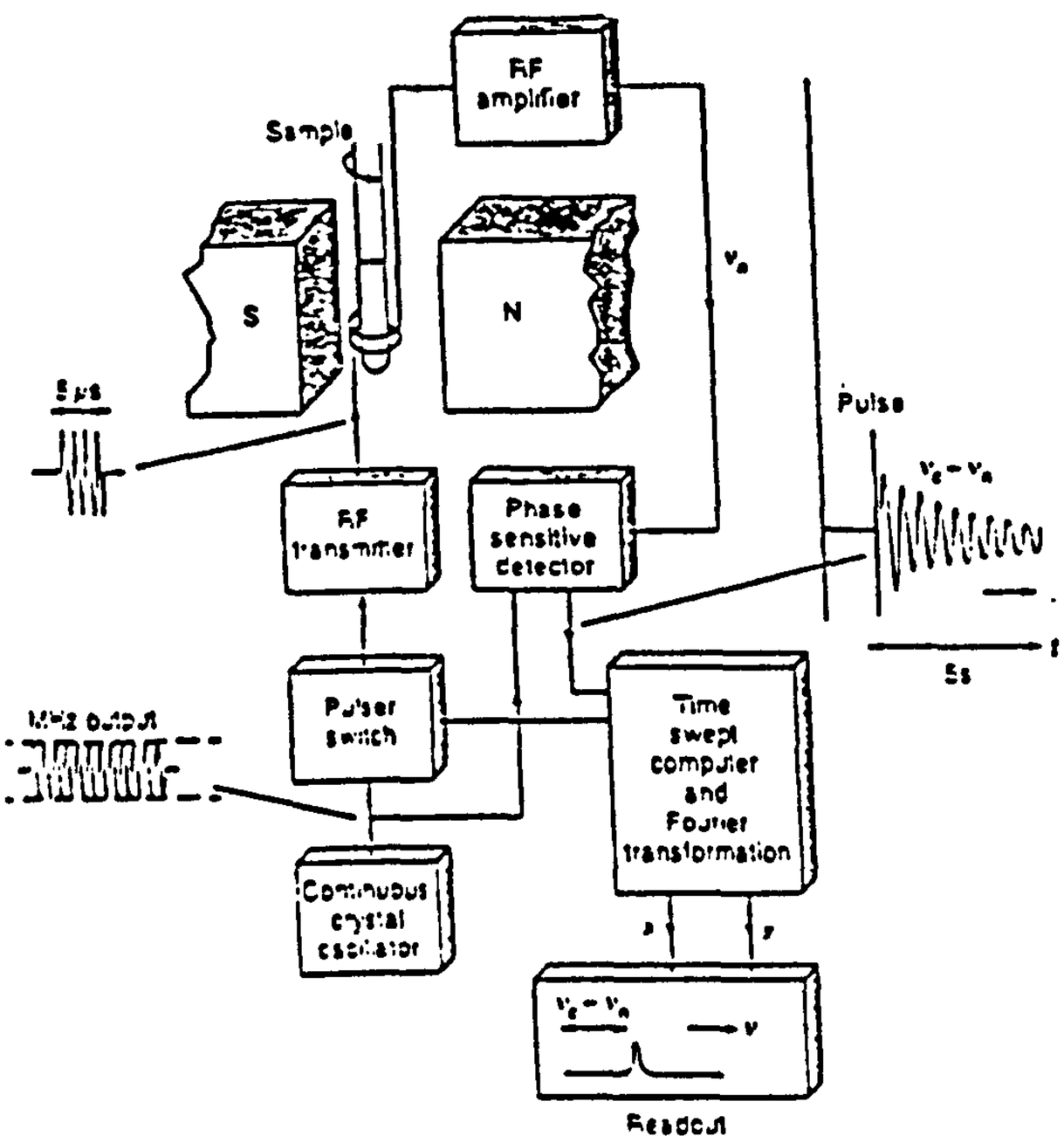


Figure 2.5: Fourier transform NMR block diagram

In this work, solid-state NMR spectra was recorded on a Bruker MSL-300 spectrometer equipped with a 7.0 T magnet in which the resonance frequencies for ^{29}Si and ^{27}Al are 59.63 and 78.21 MHz respectively.

Experimental Procedure and Calculation of Results

In this study, the technique of magic angle spinning (MAS), i.e., mechanical spinning of the sample at an angle $\theta = 54°44'$ to the external magnetic field *Bo* was applied as a routine procedure, for both ^{29}Si and ^{27}Al NMR spectra. MAS was used simultaneously

with another technique known as high-power dipolar ^{1}H decoupling (DD), which was also helpful in removing residual dipolar interactions specially for ^{29}Si spins with nearby ^{1}H nuclei. These two techniques are important to eliminate the various spin interactions that can cause line broadening in solids spectra. The typical MAS rates were in the region 4.5 Khz, and between 5,000and 16,000 transients were accumulated for each spectrum, with a recycle time between 2 to 3 s. This recycle time is sufficient to allow quantitation of the ^{29}Si resonances. For the ^{27}Al spectra MAS rates were 10 to 12 Khz and typically 12,000 transients were accumulated for each spectrum, with a recycle time of 250 ms. The chemical shifts were quoted relative to external tetramethylsilane (TMS) for ^{29}Si, and relative to 1 M aqueous aluminium nitrate solution for ^{27}Al. The quantitation of the ^{29}Si spectra was made by deconvolution of the overlapping resonances using the Brucker PC software WINNMR/WINFIT.

2.3.4 Measurement of the Consumption of CO_2 - 'Eudiometer Test'

A carbon dioxide eudiometer test is a technique designed to study the kinetics of the accelerated carbonation reaction. In this work, this technique is particularly important to help in the investigation of the effects of carbonation on the different cement/waste systems. The carbon dioxide gas is left in contact with the fresh cement-based material and its consumption is measured in real-time graphics.

Equipment

The eudiometer is formed by two main parts:

a) a syringe for measuring changes in gas volume, whose position sensor interfaces with
b) a computer which records and plots the results

A photograph of the eudiometer is shown in Figure 2.6.

The syringe is filled up with the gas and is connected to a chamber which holds a small cylindrical sample (1.5 cm X 1.5 cm) of cement/waste paste. Sample temperature is easily varied and CO_2 may be pressurised or diluted with air or other gases. The syringe

is interfaced with a computer which displays the progressive consumption of CO_2 expressed as % by weight of cement.

Experimental Procedure and Calculation of Results

The dry waste and the cement (blended or non-blended) was mixed by hand prior to the addition of water in sealable bags. Immediately after mixing, samples were submitted to a standard compaction pressure and placed in the eudiometer chamber. The work was conducted at normal atmospheric conditions in a laboratory, i.e., normal atmospheric pressure and room temperature (21°C ± 2) and a relative humidity of 55% ± 5. Samples with very high water/cement (w/c) ratio were constantly agitated by hand during carbonation to avoid sedimentation of any material at the bottom of the sample holder. The results were expressed as real-time graphics the consumption of carbon dioxide. The controlling program is shown at Appendix 1. Samples were analysed in triplicate and a 95% confidence interval was applied to estimate the range within which the true mean may be found.

Figure 2.6: Carbon dioxide eudiometer

2.4 SUMMARY

In this Chapter the main materials and tests used to study the performance of carbonated solidified hazardous wastes were presented. The following Chapters investigate the effects of carbonation on cement-solidified waste forms, discussing the influence of mix parameters, binder choice and kinetics of the carbonation reaction by examining the physico-chemical properties of the carbonated material. Chapter 3 is the preliminary study, and gives the first results in terms of metal fixation, strength and microstructural development of carbonated and non-carbonated waste forms.

CHAPTER 3

PRELIMINARY INVESTIGATION INTO THE EFFECTS OF CARBONATION ON SOLIDIFIED HAZARDOUS WASTE

3.1 PREVIEW

In Chapter 2 the materials and experimental techniques used in this work were outlined. These were used to examine physical, microstructural and chemical properties of solidified products.

This Chapter presents the results of a preliminary investigation into the effects of carbonation during solidification of an industrial waste (Cory waste) with ordinary Portland cement (OPC). This is an introductory experimental work, and has already been published (Lange et al., 1996).

The first part of this Chapter introduces the OPC/waste mix designs and curing regimes (nitrogen, air and carbon dioxide) used. Those experimental details not referred to in Chapter 2, are described in the appropriate part in this section. The remainder of the Chapter gives a comparison of the results in terms of leachate metals fixation, strength and microstructural development between samples cured in the different environments. The closing section discusses and summarises these results.

3.2 GENERAL BACKGROUND

Cement-based solidification is one of the preferred chemical treatment techniques for inorganic hazardous wastes, as already discussed in Chapter 1. Ordinary Portland cement (OPC) is often used as the biding agent on its own, or in combination with cement replacement materials (Conner, 1990).

Many wastes such as mixed organic/inorganic industrial wastes, soils contaminated with toxic metals and organic constituents, incinerator residues and bulk wastes from the

power generation industries are using solidification technology as a pre-treatment prior to disposal (Roy et al., 1992).

One waste stream which has been seen as suitable for cement-based solidification is metal plating and finishing operations wastes, and a blended material stream comprised of waste of this type was available from Cory Environmental in Essex and is used here.

The diverse nature of these wastes has highlighted many difficulties encountered during the use of solidification technology, specially by the deleterious interference of these materials with commonly binding agents, such as OPC. Examination of those materials has shown that normal hydraulic pozzolanic reactions may be significantly retarded or poisoned (Jones, 1988; Peer, 1993; Hills et al., 1994a). Although some of these materials appeared to 'set' and harden in the laboratory, there is mounting evidence to suggest that for some wastes this is a consequence of the effects of exposure to atmospheric CO_2. It has also been reported that carbonation may directly alter the chemical and physical properties of solidified waste forms (Conner, 1993).

Therefore, where hydration reactions are compromised by waste-binder interference effects it is theoretically possible for the effects of carbonation to be different from normally hydrated concrete. In such cases carbonation may be beneficial as may be demonstrated in similar systems such as the carbonation of quick lime stabilised heavy metal soils and residues (DCR Process, 1978).

It would, therefore, be useful to examine the general performance of OPC/real waste systems in the presence of carbon dioxide and to relate the results of leachate metal fixation, strength and phase development of those systems.

3.3 MATERIALS AND EXPERIMENTAL METHODS

The material (OPC, Cory Waste) and methods (UCS, X-RD and leaching test) used were described in Chapter 2.

Table 3.1 shows the mix design used. It should be noted that the variation in w/c ratio was necessary in order to maintain a fixed solid content (typically 55-65%) as used commercially.

Table 3.1: Mix designs OPC/Waste laboratory specimens

MIXES	WASTE %	OPC %	WATER %	SOLIDS %	W/C RATIO
1	0	65	35	65	0.54
2	35	20	45	55	2.25
3	35	30	40	65	1.33
4	35	25	35	60	1.40

The dried ground waste was mixed with cement and distilled water for three minutes using a planetary mixer. Cylinders with dimensions of 50 mm x 50 mm were cast in PVC moulds and immediately placed in climate-controlled containers and allowed to mature for 28 days, under the following three conditions: (1) air (bench laboratoty); (2) carbon dioxide; (3) nitrogen. After five days, the cured cylinders were demoulded and returned immediately to their respective containers.

The carbon dioxide environment was maintained at a 50% relative humidity as described in Chapter 2. The climate container was purged of air and stabilised by passing the CO_2 at 5 ml/min during 10 minutes. The container was submitted periodically to this regime to avoid carbon dioxide starvation. The temperature was maintained between 20°C and 23°C. The nitrogen samples were stored under a dynamic system, where the nitrogen was allowed to flow slowly through a closed container holding the samples under the same temperature conditions.

Samples were then tested for leaching characteristics, strength and phase development.

3.4 RESULTS

3.4.1 Strength Development

As might be expected, strength increases with the amount of OPC in the mix. Figure 3.1 shows the strength development of all mixes at 28 days.

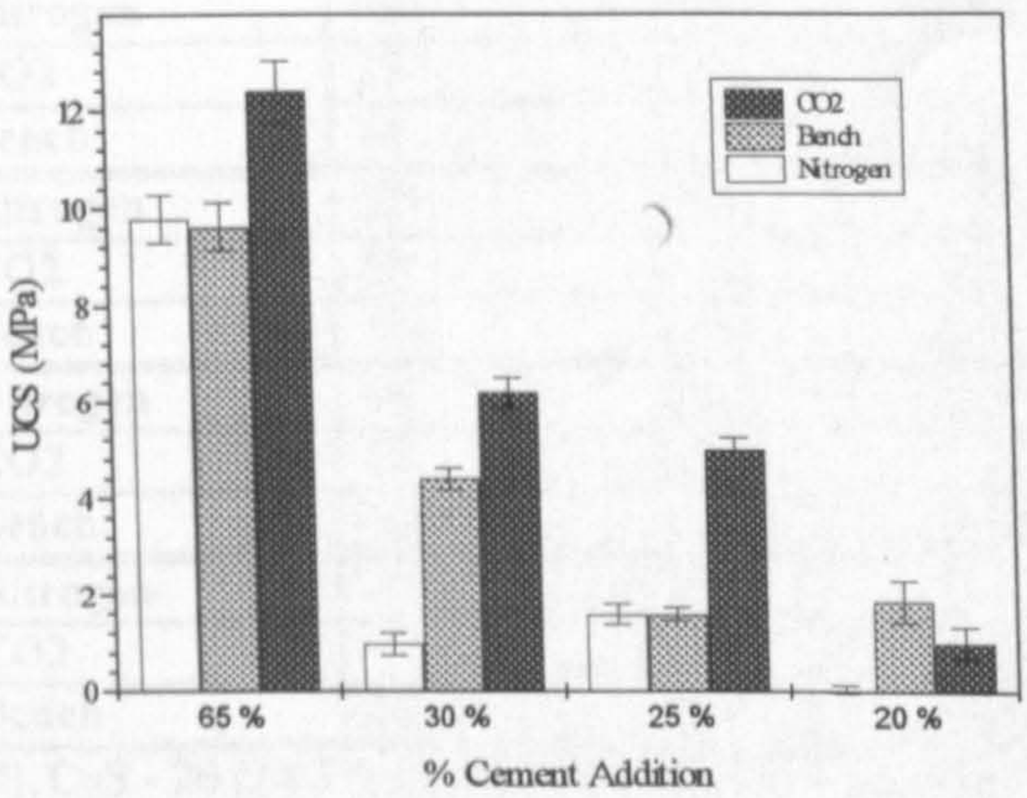


Figure 3.1: Strength development at 28 days

The control samples without waste addition (65% OPC w/w) gave the highest strength value of 12.38 MPa for the CO_2 cured sample. The nitrogen and bench cured specimens had similar strengths at approximately 10 MPa. However, when waste was included in the mixtures this relationship changed.

The nitrogen cured samples gave the lowest strengths for all waste additions. At the lowest OPC content the strength recorded was well below acceptable limits in that the samples examined were only just self supporting. The samples cured in CO_2 gave higher strengths for 30 and 25% OPC contents but a lower value at the 20% OPC content.

3.4.2 Phase Development

Table 3.2 shows the main crystalline phases identified in the samples at 28 days of age.

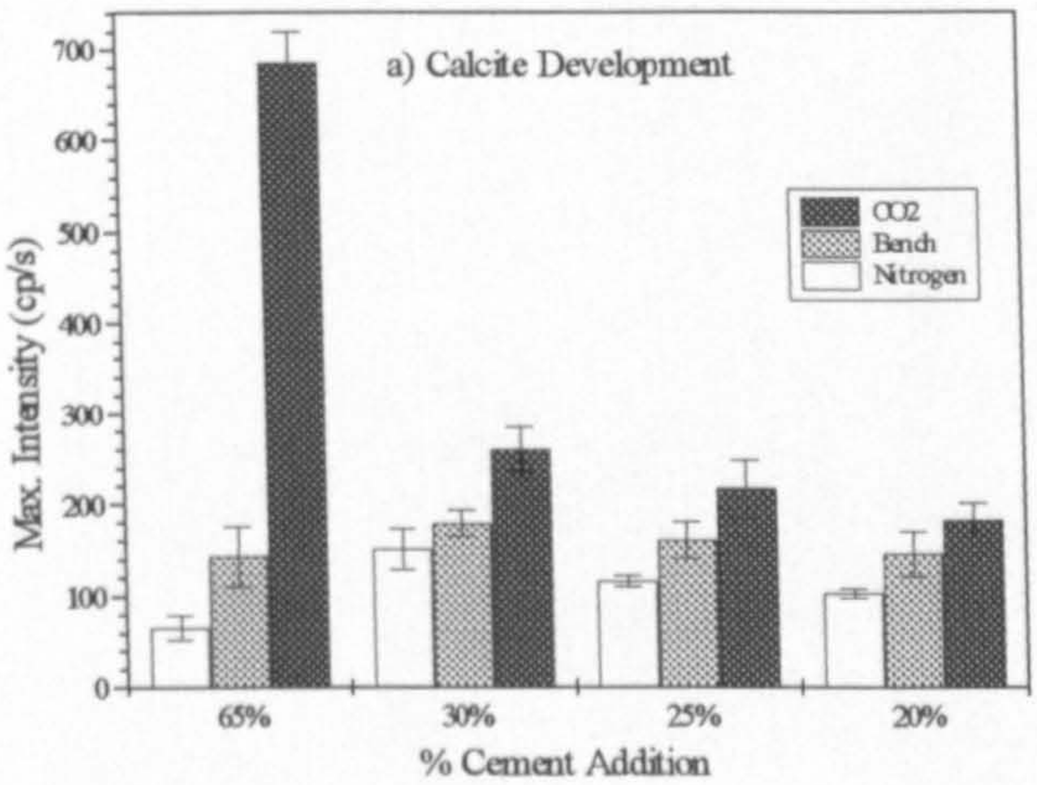
Table 3.2: Intensity of X-Rays (cp/s) recorded for solidified waste forms

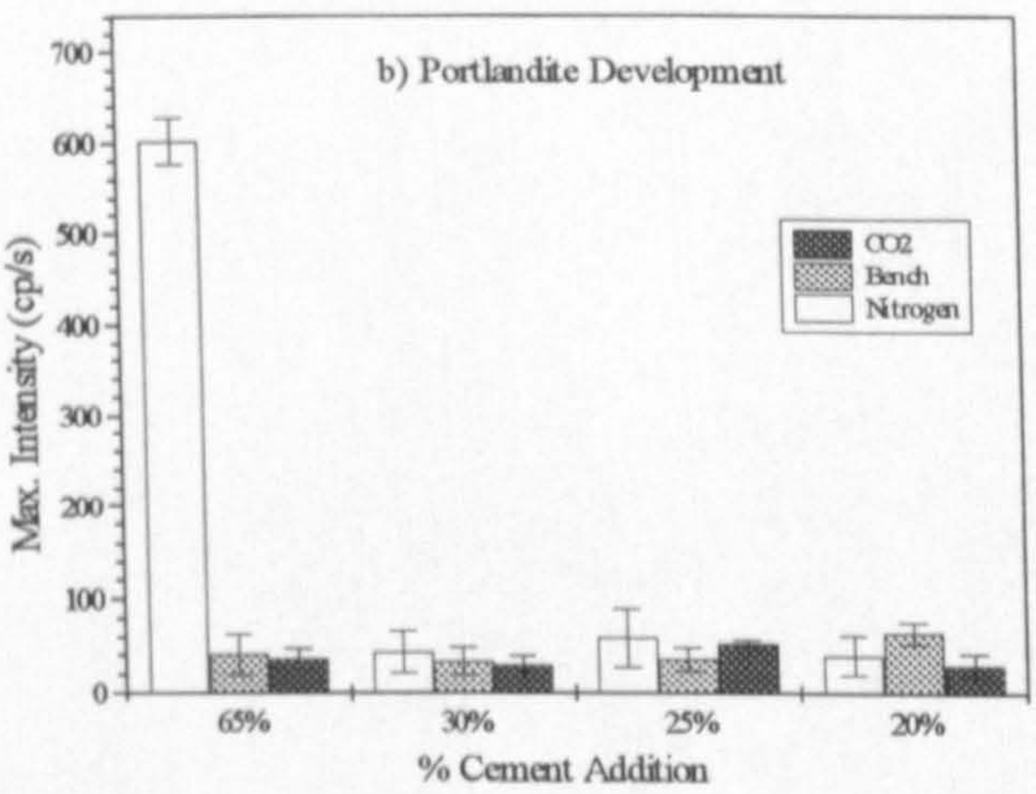
Phase Dev.	Atm. Exposure	65% OPC	30% OPC	25% OPC	20% OPC
	Nitrogen	67	152	118	104
Calcite	CO2	686	261	217	183
	Bench	144	180	161	146
	Nitrogen	603	45	60	41
Portlandite	CO2	37	31	54	31
	Bench	42	35	37	65
	Nitrogen	227	83	72	60
C3S	CO2	59	56	54	22
	Bench	160	115	103	38
	Nitrogen	56	295	367	46
Gypsum	CO2	58	38	326	106
	Bench	108	328	348	79
	Nitrogen	135	140	122	51
Ettringite	CO2		42	150	61
	Bench	60	56	53	50

Note: Calcite - 2θ (29.5°), C_3S - 2θ (34.5°), Portlandite - 2θ (18.35°), Gypsum - 2θ (11.4°) and Ettringite - 2θ (9.7°).

Phase development, which is estimated by comparing peak intensities of the principal diffraction lines differs for each set of samples. In the bench cured samples, portlandite, calcite and ettringite can be readily distinguished. The nitrogen cured samples were largely devoid of portlandite but contained larger quantities of ettringite and unhydrated C_3S. In the CO_2 cured samples calcite, portlandite and gypsum were important constituents while ettringite was not detected in all samples, including the control. The background intensities recorded were similar for all samples.

The influence of the carbon dioxide curing environment on modifying the hydration of the OPC is illustrated in Figure 3.2a-c.





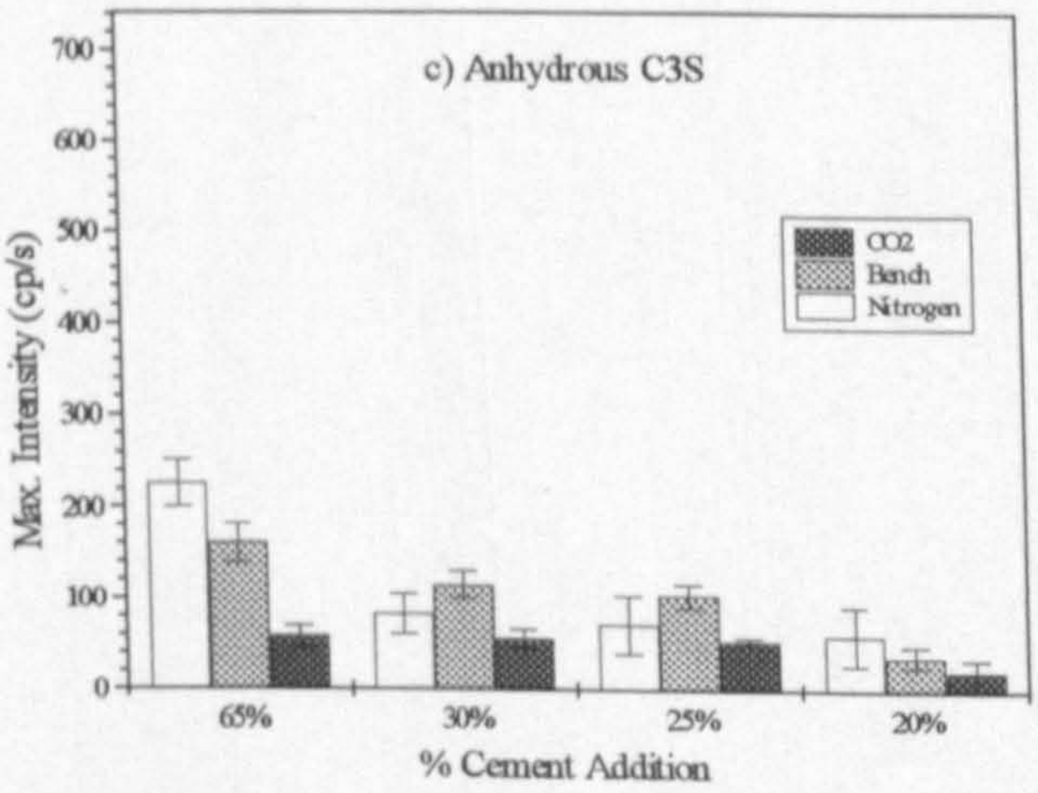


Figure 3.2: a) Calcite development, b) Portlandite development and c) Anhydrous C_3S

Figure 3.2-a shows the gradual increase in the development of calcite in all mixes, according to the following: CO_2 > Bench > N_2. There also appears to be an inverse relationship between the X-ray intensities of calcite and C_3S, as shown in Figure 3.2-c.

Figure 3.3a-c show the intensity of X-rays recorded for gypsum, and ettringite for the three curing environments and indicate that the latter phase appears to decompose in the presence of CO_2 with a consequent increase in the proportion of calcite and gypsum in the product.

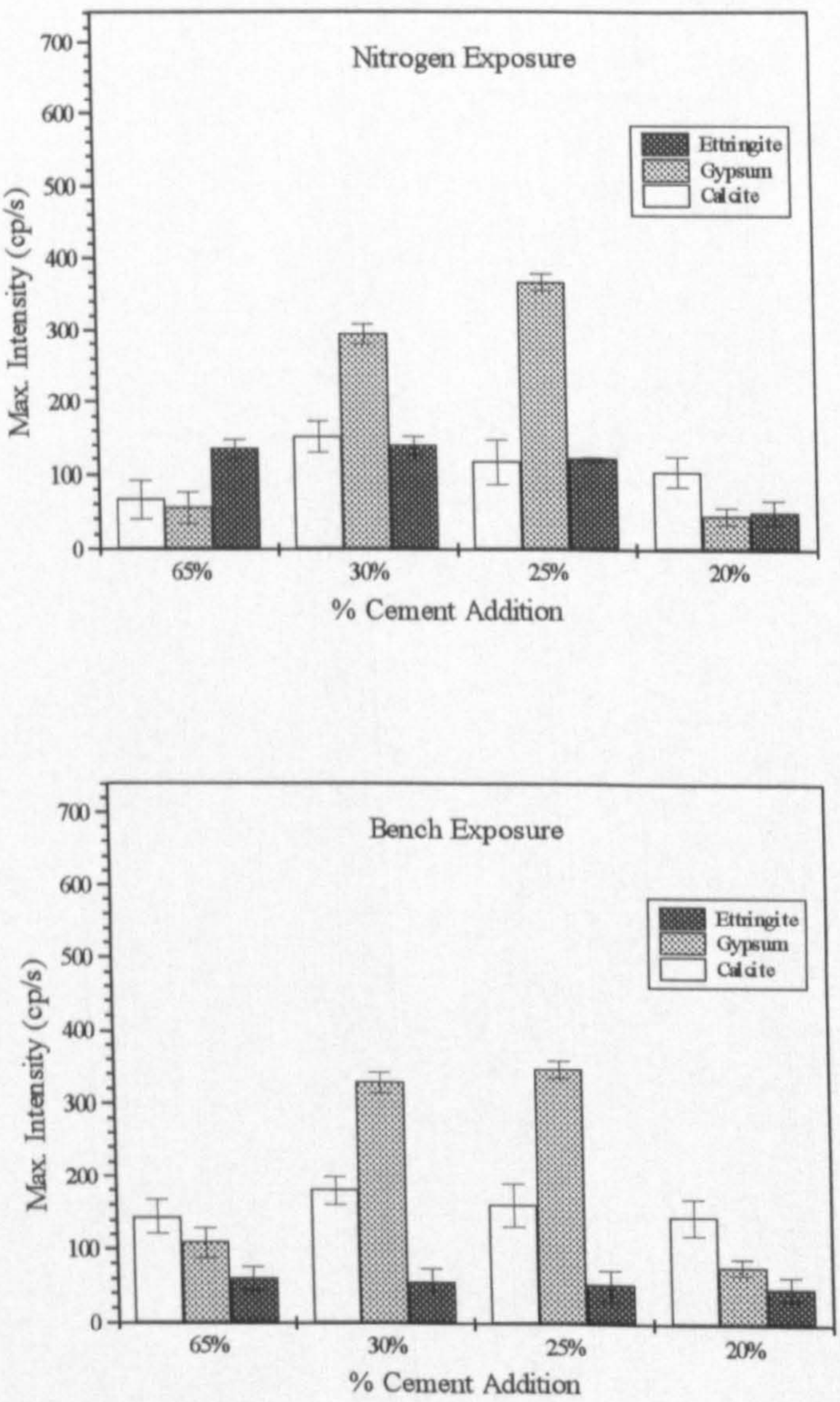


Figure 3.3a-b: Gypsum, ettringite and calcite development in different environments

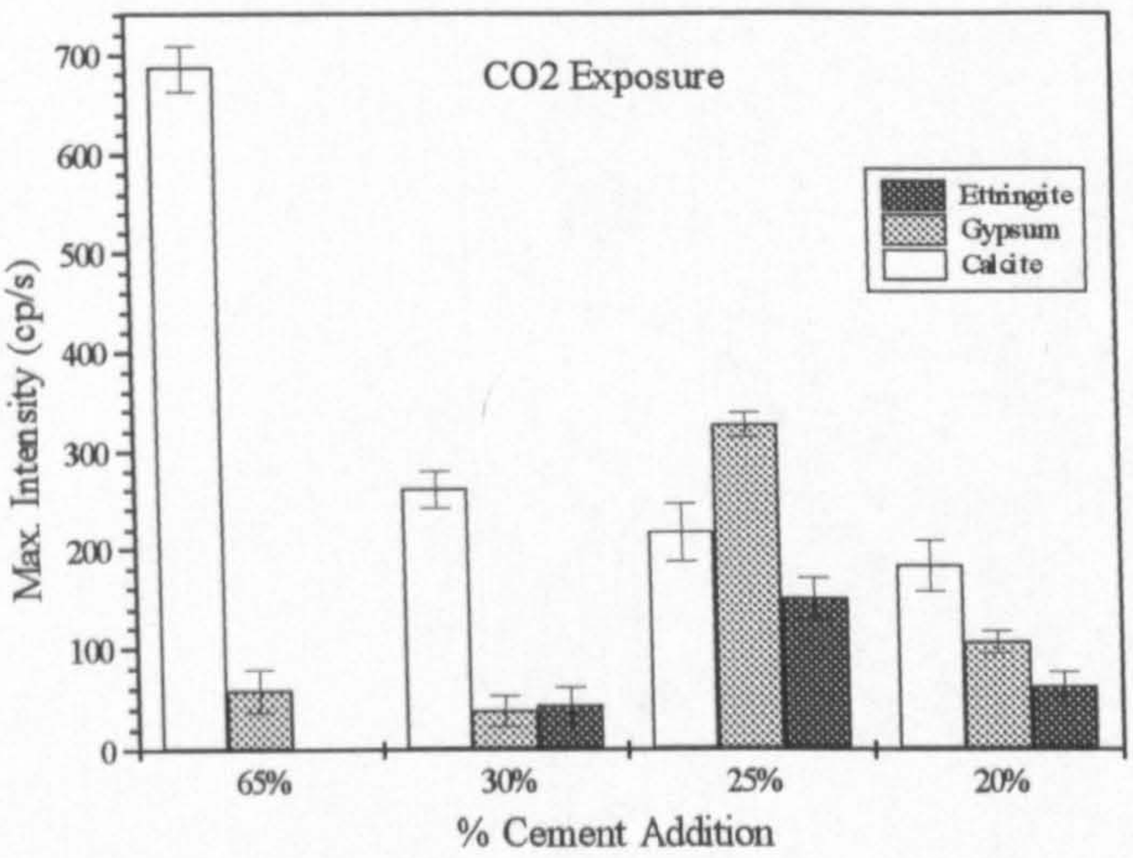


Figure 3.3c: Gypsum, ettringite and calcite development in different environments

3.4.3 Leaching Characteristics

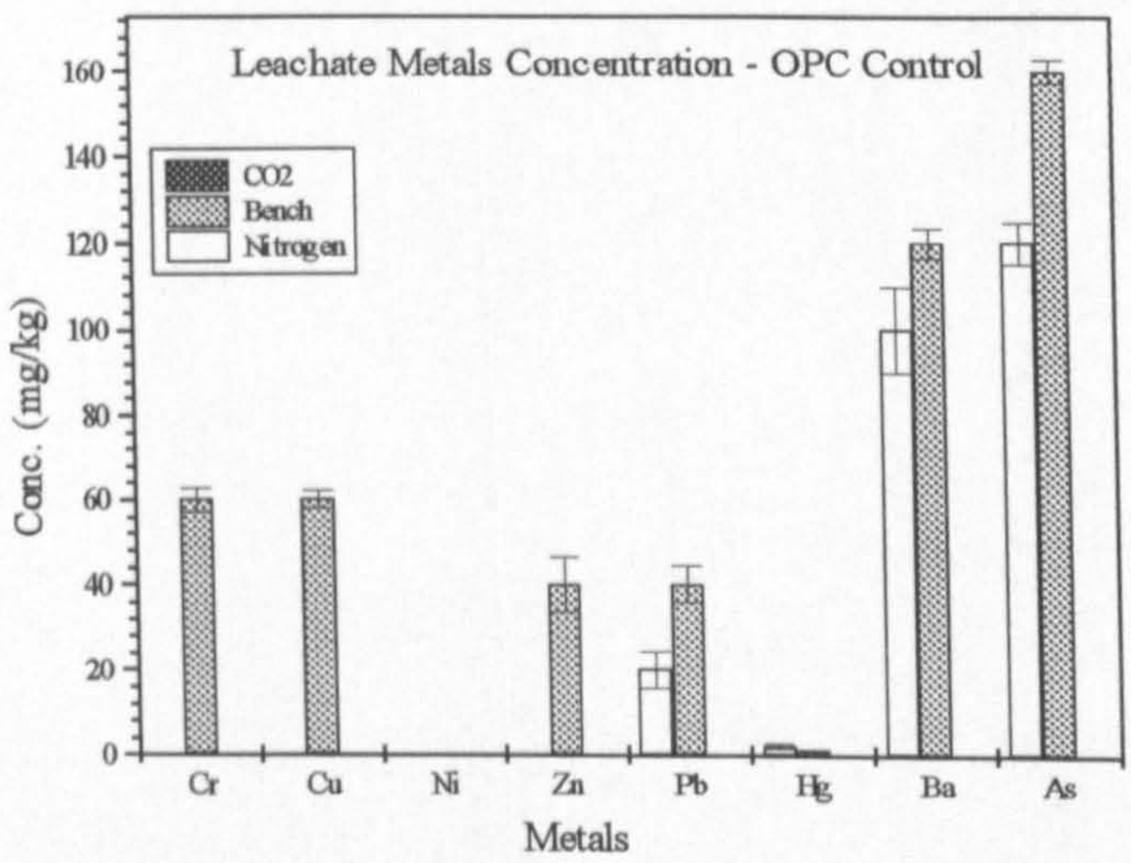
Table 3.3 gives the metal concentrations in the leachates from the samples cured in the three environments.

Table 3.3: Leachate metals concentrations (mg/kg)

Mix	CaO	Hg	Cr	Cu	Mn	Ni	Pb	Zn	Cd	Ba	As
1N	13.0	2	< 1	<1	<1	<1	20	<1	<1	100	120
2N	3.8	7	260	60	<1	20	20	20	<1	60	80
3N	4.6	6	100	20	<1	20	20	20	<1	80	80
4N	6.4	12	200	40	<1	20	20	20	<1	80	80
2C	18.0	3	380	60	<1	60	<1	<1	<1	20	220
3C	4.2	3	233	60	<1	20	<1	<1	<1	40	147
4C	11.0	5	460	60	<1	60	<1	<1	<1	20	160
1B	19.4	1	60	60	<1	<1	40	40	60	120	160
2B	23.8	15	680	140	<1	100	<1	<1	<1	20	220
3B	22.8	23	520	40	<1	80	<1	<1	<1	40	200
4B	22.3	31	500	73	<1	53	<1	<1	<1	47	167

Obs.: CaO in %. Sample 1C results not available.
N= nitrogen; C= carbon dioxide; B= bench (air). All at normal atmosphere pressure

For clarity these results are represented as histograms for the different levels of OPC addition (Figure 3.4). The bench cured samples gave the highest readings for a range of metals (Cr, Cu, Zn, Pb, Hg, Ba and As). The CO_2 cured samples presented lower values, whereas nitrogen curing provided the lowest leachate metal levels for all levels of OPC addition.



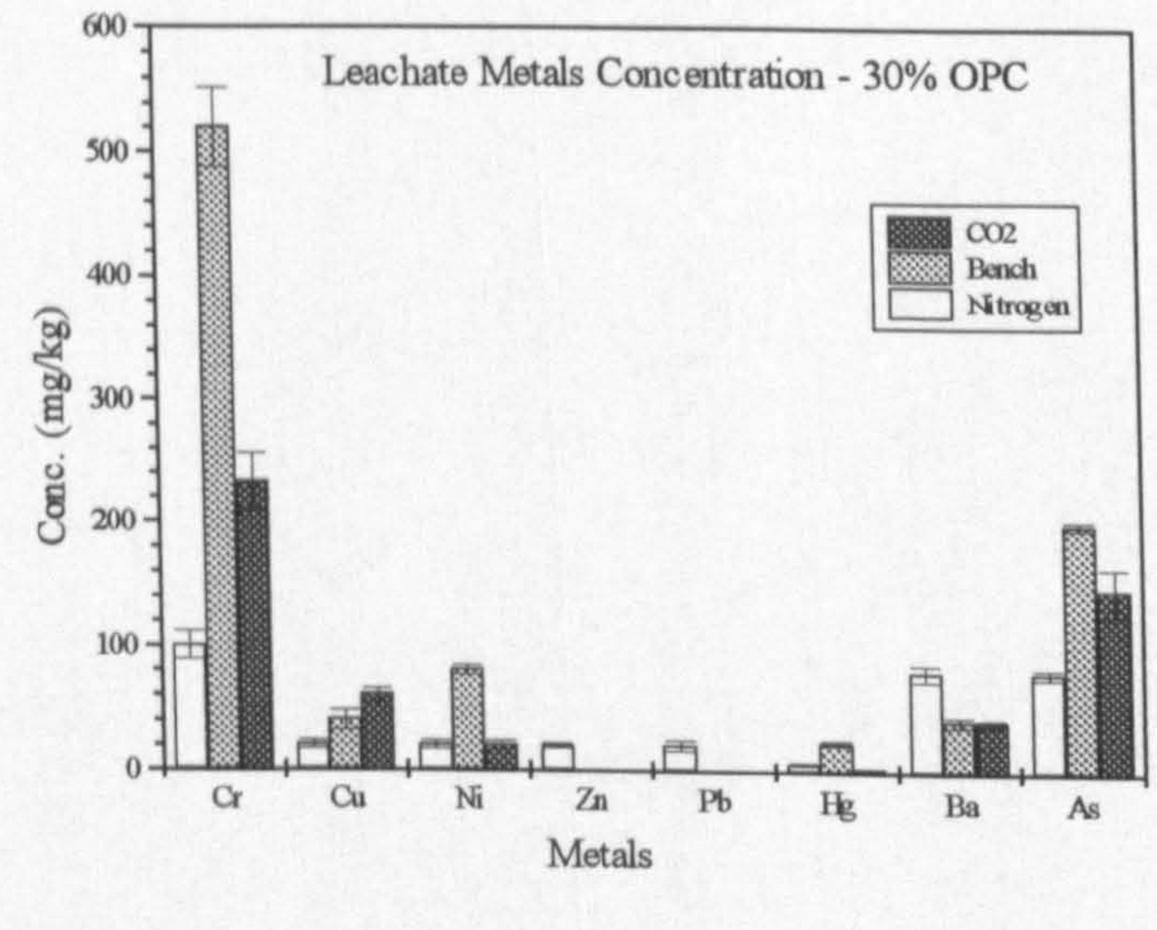
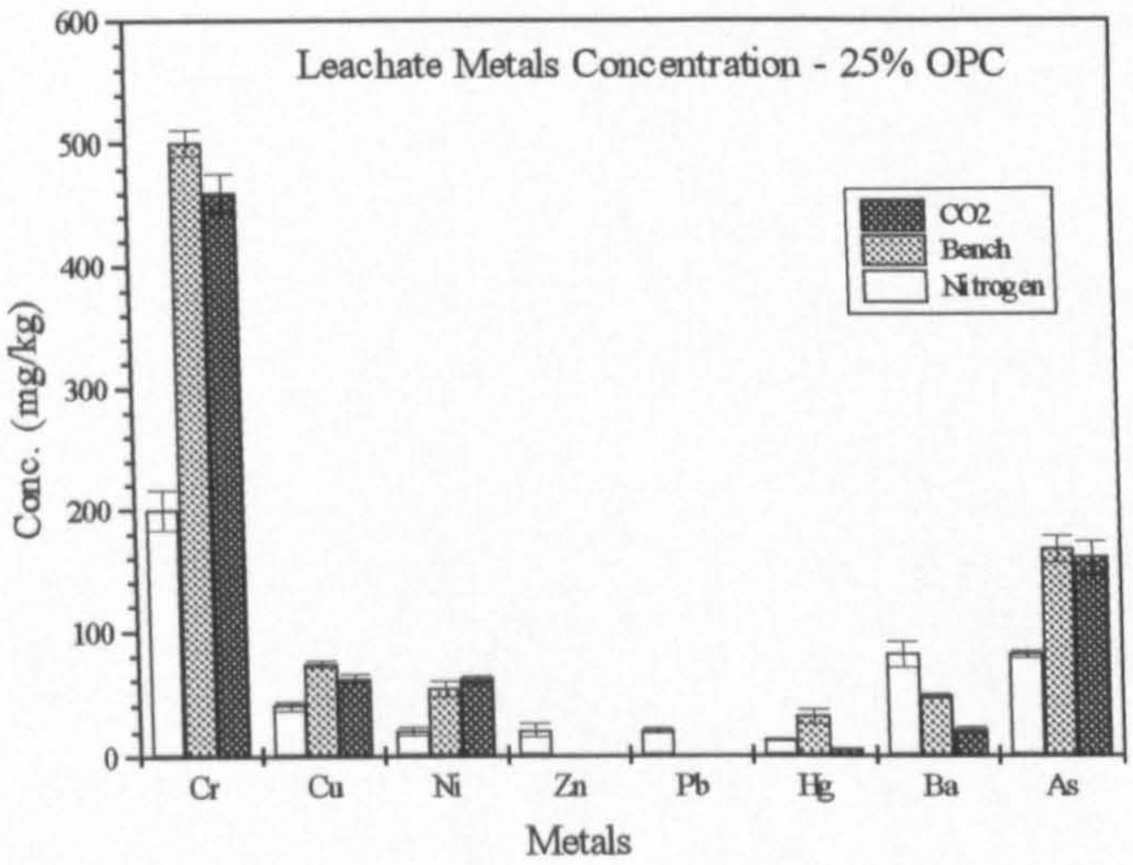


Figure 3.4: Leaching characteristics



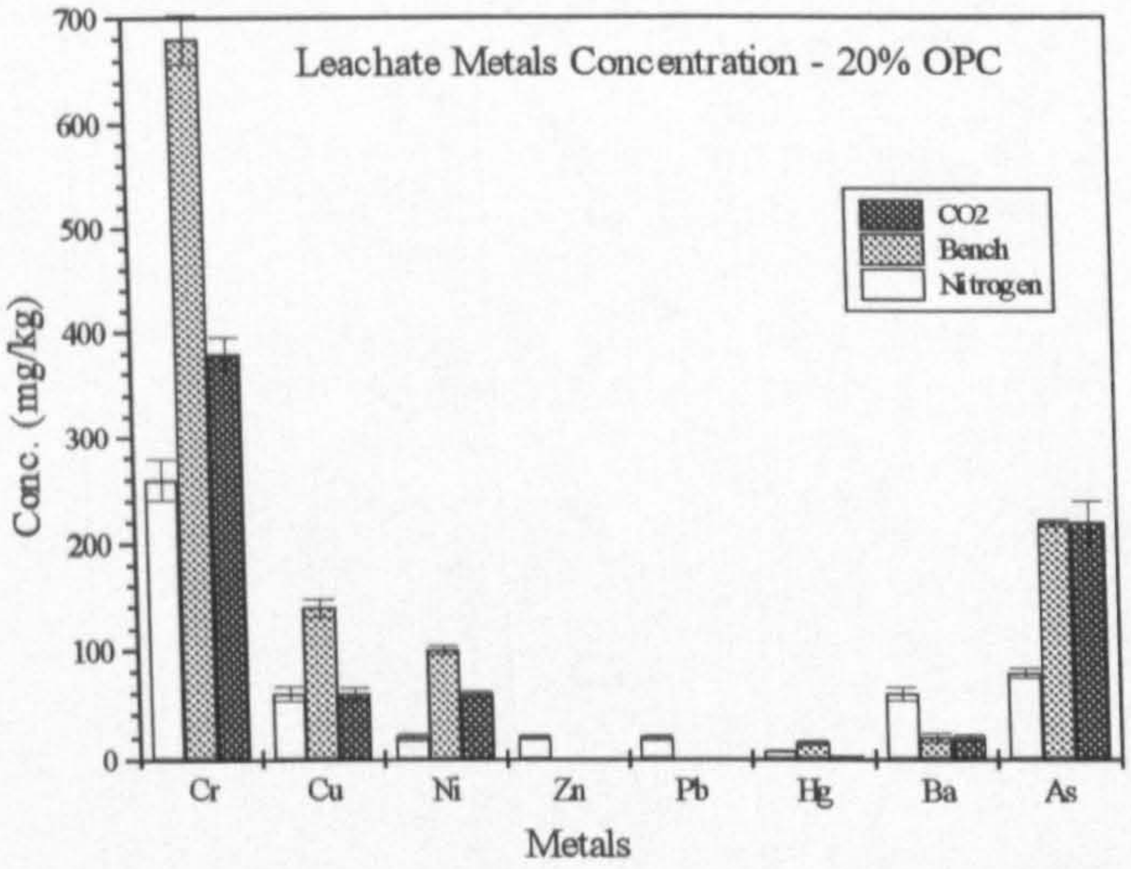


Figure 3.4: Leaching characteristics

3.5 DISCUSSION

The effects of carbonation on solidified waste forms are different from those on structural quality concrete as they may be beneficial and not deleterious. This observation primarily arises from the increased metal binding capacity and improved structural properties of the solidified waste forms and is explored in more details in the following Chapters.

In the present study, the most obvious effect upon waste forms is on strength. The improvements realised result from the increase in hydration of C_3S driven by the

formation of calcium carbonate and which is clearly illustrated in Figure 3.5 where the amount of anhydrous alite can be seen to be much lower in carbonated samples.

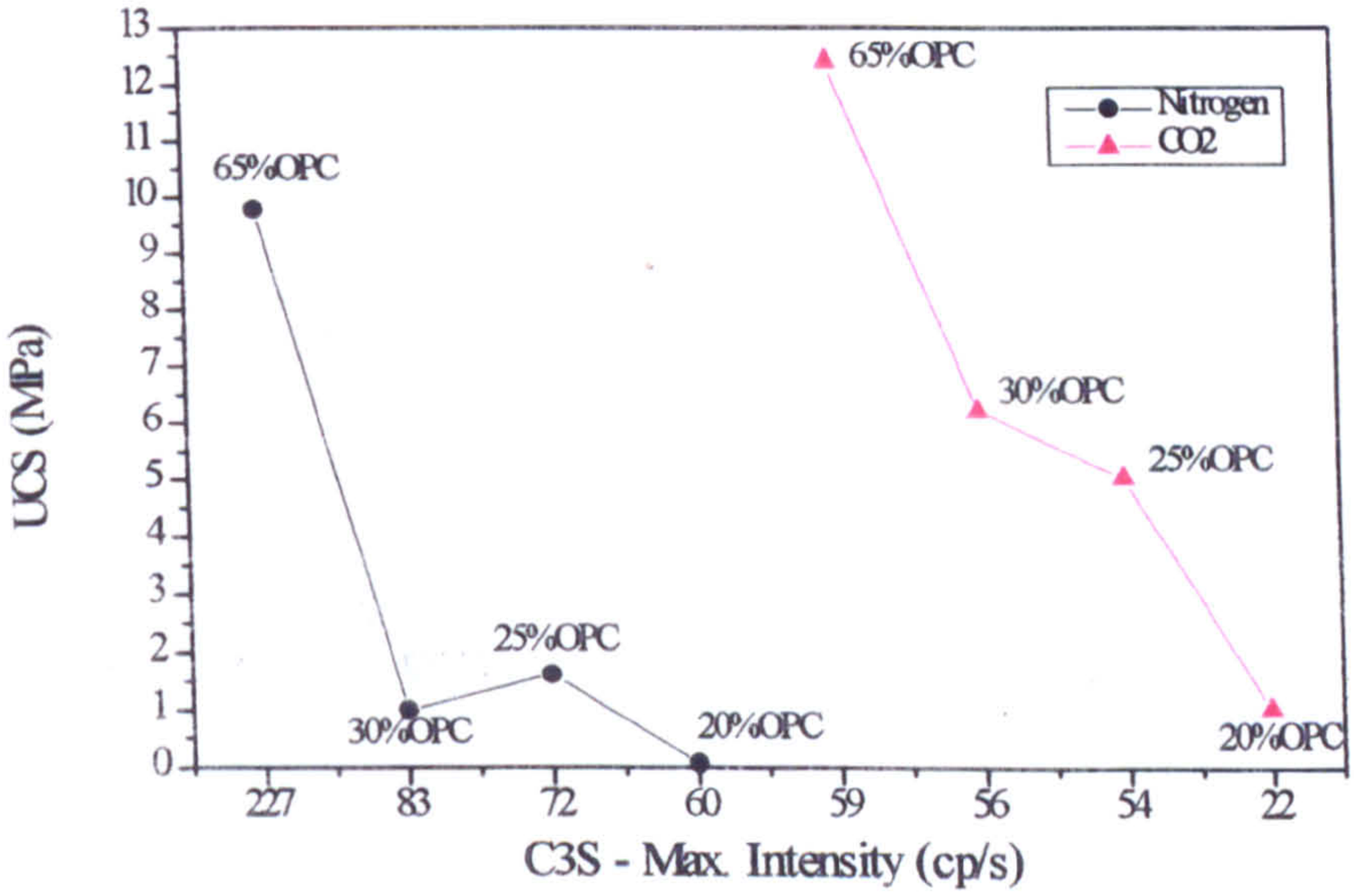


Figure 3.5: Relationship between the amount of anhydrous C_3S and strength development

Examination of waste forms by XRD (Figures 3.2 a-c) show that it is possible to closely observe the relationship between C_3S hydration and the formation of calcite. This relationship suggests that for the beneficial effects of carbonation to be fully realised an optimised cement level has to be maintained. However, this optimum may be cement specific depending on the waste materials to be treated as a result of interference due to waste/binder interactions (Hills et al., 1994a).

The phase development displayed in waste forms can be seen to be dependant upon the curing environment. For example, the nitrogen cured samples were essentially devoid of hydration related phases save for a trace amount of CH which probably formed during mixing. On the other hand in waste forms where calcite, gypsum and ettringite were present together complete carbonation had not taken place. This can be illustrated with reference to equation 3.1, given below, where ettringite decomposes in the presence of moisture to give calcite and gypsum (Nishikawa et al., 1992). Upon completion of the reaction, ettringite, which has been recognised as an important

solidified waste materials, is replaced by these phases and which may continue to structurally stabilise the waste form.

$$3CaO.Al_2O_3.3CaSO_4.32H_2O + 3CO_2 \rightarrow 3CaCO_3 + 3(CaSO_4.2H_2O) + Al_2O_3.xH_2O + (26\text{-}x)H_2O \quad \text{(Eq.3.1)}$$

ettringite calcite gypsum aluminum gel

The factors that control the production of leachate are complex and interrelated. In this work, however, the effects of carbonation appear to be beneficial and this is probably a result of several aspects of the carbonation reaction. It is generally recognised that the buffering capacity of waste forms is related to the ability of, for example, C-S-H and CH to maintain pH. Therefore, it might be expected that those waste forms where normal hydration has proceeded have improved leaching performance over those where, for example CH might be absent. This proved not to be the case in the testing regime employed as was seen when the leaching results from bench cured samples are compared with CO_2 cured mixes in spite of the ability of CO_2 to lower local pH conditions by 3 units or more. This in turn suggests that pore modification, and perhaps, precipitation of salts containing toxic species also had an important effect.

The results from the nitrogen cured mixes do, however, clearly illustrate the benefits of stabilising a waste prior to treatment with OPC. In these samples hydration did not proceed and the waste maintained the optimum pH conditions of the sludge and this manifested itself with improved leaching results.

The leachate analysis also shows an adequate reduction in metal concentration compared to the raw waste. Carbonation has been seen to influence the properties of cement solidified waste forms in a number of ways. For example, C-S-H gel products, which are recognised as playing an important role in the fixation of toxic species, are significantly altered. This manifests itself as a change in the ion exchange capacity of the gel (Richardson et al., 1993; Cocke at al., 1993) as carbonation proceeds. The gel becomes progressively polymerised as OH and Ca are consumed in the production of $CaCO_3$ despite the apparent maintenance of morphology (Sauman, 1972; Suzuki et al., 1985).

Portlandite which may be present in abundance within hydrated cement containing materials also directly reacts with CO_2 to produce calcite. The volume change accompanying this reaction can help to fill pore space, densify the product and improve structural integrity. In addition the direct nature of this particular reaction may lead to the precipitation of calcium metal double carbonates such as calcium zincate when certain toxic species are present in solution (Mollah et al., 1993).

3.6 SUMMARY AND CONCLUSIONS

In this Chapter, the results of an initial study relating to the effects of carbonation on solidified cement-based waste forms has shown that carbonation plays an important role in accelerating the apparent hydration of binder within the solidified waste-forms. The results of carbonation of the solidified products were characterised by enhanced calcite contents, higher strength values, and a significant reduction in leachable metals extracted when compared to air-cured samples. Samples cured under a nitrogen atmosphere showed significant retardation of hydration, resulting in low strength values but improved fixation of certain leachable metals.

Carbonation clearly produces physical and chemical changes in the microstructure of cement-based materials that result in increased metal binding capacities. Nevertheless, questions have arisen regarding the nature of the hydration between the presence of calcite and the hydration and setting of the cement paste and the effects of carbonation upon different waste/binder systems, i.e., different cement types, mineral admixtures and waste materials. These are explored further in the following Chapters.

CHAPTER 4

THE EFFECT OF CARBONATION ON THE PROPERTIES OF BLENDED AND NON-BLENDED CEMENT SOLIDIFIED WASTE FORMS

4.1 PREVIEW

In Chapter 3 a preliminary investigation into the effects of carbonation on a commercially solidified hazardous waste was undertaken. The waste forms produced were cured in a carbon dioxide atmosphere contained greater amounts of calcite which increased with increasing cement addition. Unconfined compressive strength was higher for samples cured in CO_2 environment and this could be attributed to the higher intrinsic strength of calcite over portlandite and an improved microstructure. In general, an improved fixation of metals in carbonated systems was observed, and was attributed to a lowered porosity within the matrix and a possible formation of insoluble complex metal salts. Overall, these preliminary results indicated some beneficial effects of carbonation upon the solidified waste and that the physico-chemical properties of carbonated materials are distinct. The most common binder currently used in cement-based solidification is OPC, and as a consequence consideration of the effects of carbonation on different binders (blended and non-blended) must also be addressed.

Thus, the aim of this Chapter is to examine the effects of carbonation on the mature properties of two blended inorganic industrial wastes bound to different blended binders. The current understanding of hydration of Portland and calcium aluminate cements as well as the carbonation phenomenon on these cementitious materials are discussed. Waste forms are prepared and cured in three different environments: nitrogen, air and carbon dioxide for 28 days when the strength development, microstructural development and leachate metal fixation are examined. The Chapter concludes with a discussion which shows that the choice of the type of cement or blended cement system can be optimised when fixation of waste species in a carbonated product is concerned.

4.2 GENERAL BACKGROUND

OPC type cements are dominated by silicate phases which form some 85% of the anhydrous material. The two most important products formed from the hydration of tricalcium silicate (C_3S) and β-dicalcium silicate (β-C_2S) are calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). C-S-H is an amorphous or poorly crystalline gel product produced by the generalised reaction described in Eq. 4.1 (Taylor, 1990).

$$6Ca^{2+}_{(aq)} + 5HSiO_3^-(aq) + 7OH^-(aq) \rightarrow 6CaO.5SiO_2.6H_2O \qquad \text{(Eq.4.1)}$$

The hydration of OPC is affected by the presence of carbon dioxide and this may lead to deleterious effects in structural concrete. This results from a hydration of $CO_{2\,(aq)}$ leading to the formation of H_2CO_3, HCO_3^-, CO_3^{2-} which takes place almost instantaneously, lowering the pH locally by 3 or more units (Maries, 1992), leading to eventual depassivation of steel reinforcement.

The pore volume of carbonated cement paste changes as a result of the conversion of CH to calcite and decalcification of C-S-H gel. The volume change accompanying this reaction can help to fill pore space, densify the product and improve localised structural integrity. The removal of calcium from C-S-H during carbonation results in a highly polymerised silica gel which is acid stable and maintains the same morphology as the original calcium silicate hydrate. This 'stable' silica structure may actually improve chemical bonding of certain metal cations with the components of cement matrix (Mollah et al., 1993).

The amount of aluminate phases present depend on the cement type. C_3A, the main aluminate phase present, hydrates to AFt, and the most important AFt phase is ettringite. Ettringite is sometimes the main phase formed during the solidification of waste forms and promotes an early age strength, but other metal cations may replace the Ca^{2+} or Al^{3+} or both in the compounds' structure. This substitution may be a distinct fixation mechanism for certain solidified waste species, as discussed by Hassett and McCarthy

(1992). Ettringite also decomposes in the presence of CO_2 to give calcite, gypsum and alumina gel, as already shown in equation 3.1 (Nishikawa et al., 1992).

Calcium aluminate cements are also subject to carbonation despite the general absence of CH and C-S-H phases. These cements, which are not as popular as OPC for solidification technology, are relatively expensive, but may have certain advantages when used for solidification of metallic waste. Calcium aluminate cements introduce rapid strength gain and have a high resistance to chemical attack. However, the chemistry and mechanism of carbonation both differ from OPC. Under normal conditions no portlandite (CH) is formed but the phenomenon, known as conversion, which involves the transformation of the meta-stable hydrates CAH_{10} and C_2AH_8 to stable C_3AH_6, as is indicated by Equation 4.2 and 4.3, may cause 'structural' instability when the water/cement (0.4 w/c) ratio and temperature is above certain limits.

$$3(CaO.Al_2O_3.10H_2O) \rightarrow 3CaO.Al_2O_3.6H_2O + 2(Al_2O_3.3H_2O) + 18H_2O \quad \text{(Eq. 4.2)}$$

$$3(2CaO.Al_2O_3.8H_2O) \rightarrow 2(3CaO.Al_2O_3.6H_2O) + Al_2O_3.3H_2O + 9H_2O \quad \text{(Eq. 4.3)}$$

Monocalcium aluminate (CA), is the major anhydrous phase and hydrates at low temperatures (<20°C) to form CAH_{10} and AH_x gel which in the presence of $C_{12}A_7$ leads to the formation of some C_2AH_8 (Lea, 1970). C_2AH_8 appears as hexagonal plates and on exposure to CO_2, $3CaO.Al_2O_3.CaCO_3.11H_2O$ is formed. In addition, the formation of calcite in this binder can be facilitated by the presence of alkali carbonates, which may be present in a waste according to the equation 4.4 (Montgomery et al., 1993):

$$K_2CO_3 + CaO.Al_2O_3\ aq \rightarrow CaCO_3 + K_2O.Al_2O_3 \quad \text{(Eq. 4.4)}$$

In chapter 3, it was shown that carbonated OPC/ waste systems can have improved properties over non-carbonated systems. In this Chapter, five different types of cement, i.e., ordinary Portland cement (OPC), white Portland cement (WOPC), rapid hardening

Portland cement (RHPC), sulphate resisting Portland cement (SRPC) and calcium aluminate cement (CAC) and two pozzolans (PFA and SF), are used to examine the influence of carbonation on the properties of the two industrial wastes previously described.

4.3 MATERIALS AND EXPERIMENTAL METHODS

The materials (OPC, WOPC, RHPC, SRPC, CAC, PFA, SF, Cory waste - W1 and Metal Colours waste - W2) and test methods used (UCS, X-RD, leaching test) were described in Chapter 2. These binders were selected to cover as wide a range of commonly available chemical and mineralogical compositions as possible. Table 4.1 shows the mix designs employed. Control (waste-free) mixes were also prepared using the same binders.

Table 4.1: Mix designs

Mix	*Waste %	Cement %	Admixtures %	Water %	W/C
1	30	30 OPC	-	40	1.3
2	30	30 RHPC	-	40	1.3
3	30	30 SRPC	-	40	1.3
4	30	30 WOPC	-	40	1.3
5	30	30 CAC	-	40	1.3
6	30	28 OPC	2 SF	40	1.4
7	30	20 OPC	11 PFA	40	2.0
8	30	28 RHPC	2 SF	40	1.4
9	30	20 RHPC	11 PFA	40	2.0
10	30	28 SRPC	2 SF	40	1.4
11	30	20 SRPC	11 PFA	40	2.0
12	30	28 WOPC	2 SF	40	1.4
13	30	20 WOPC	10 PFA	40	2.0
14	30	28 CAC	2 SF	40	1.2
15	30	20 CAC	10 PFA	40	2.0

Note: The same mix designs were used for both wastes. In the text Cory waste will be referred as W1 and Metal Colours waste as W2.

The dried ground wastes were mixed with the different binders and distilled water for three minutes using a planetary mixer. Cylinders with dimensions of 32mm x 32mm were cast in PVC moulds and immediately placed in atmosphere-controlled containers and allowed to mature for 28 days under the following three conditions:

1. normal atmospheric/laboratory conditions (bench)
2. carbon dioxide atmosphere
3. nitrogen atmosphere

The climate containers were maintained as described in Chapter 3, section 3.3. Samples were then tested for leaching characteristics, strength and phase development.

4.4 RESULTS

4.4.1 Strength Development

The unconfined compressive strength results are given in Figure 4.1 for the cement pastes only, the cement/waste and the cement/waste/admixtures in three different environments. The estimated standard deviation is indicated as error bars. As might be expected, the cement paste only samples gave the highest recorded strength. CAC had a strength recorded at 39.1 MPa in CO_2 atmosphere and was registered as the highest value, while the lowest strength was registered for WOPC at 17.5 MPa. The same trend for the five cements were followed in the each of the different curing environments. They are: CAC>RHPC>SRPC>OPC>WOPC.

However, when waste was included in the mixtures the relationship changed. W2 followed the same trend as the control samples but with a considerable decrease in strength values by, for example, up to 75% for CAC. For W1, RHPC gave the highest strength for all three environments, and the following trend was observed: RHPC>CAC>WOPC>SRPC=OPC.

The addition of SF and PFA in the presence of waste caused some change in strength development of different cements. For W1, silica fume particularly improved the

strength of samples in which CAC was used (9.04 MPa), followed by SRPC (8.0 MPa). PFA addition was found to cause a decrease in 28 days strength by as much as 50-60% for all cement/waste designs, with two exceptions: the SRPC and WOPC/waste mixes when cured in a nitrogen atmosphere. For W2, silica fume improved remarkably the strength value of the OPC/W2 sample cured in CO_2 by up to 92%. The addition of PFA, in general, caused a decrease in strength values for all systems.

For all mix designs, nitrogen-cured samples gave the lowest strength. For cement paste only, a reduction of strength, compared to CO_2 cured samples, of up to 40% was noted. Whereas for cement paste/waste addition and cement paste/waste/SF/PFA a reduction of 70% (W1) and 62% (W2); 53% (W1) and 38% (W2) respectively were recorded. The results clearly indicate that these differences result from the curing environment employed.

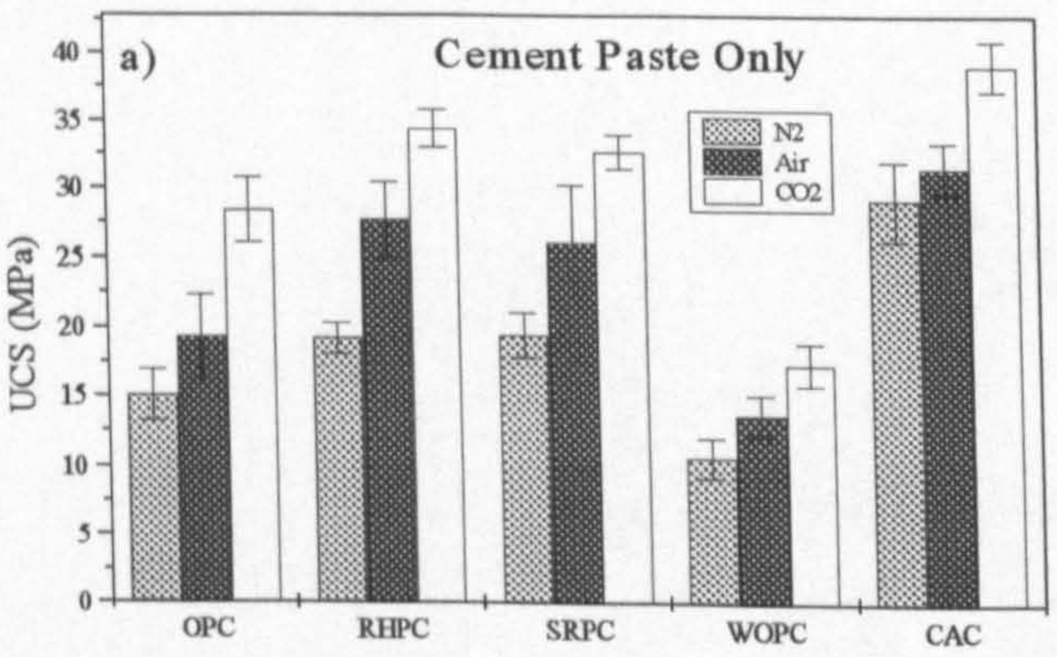
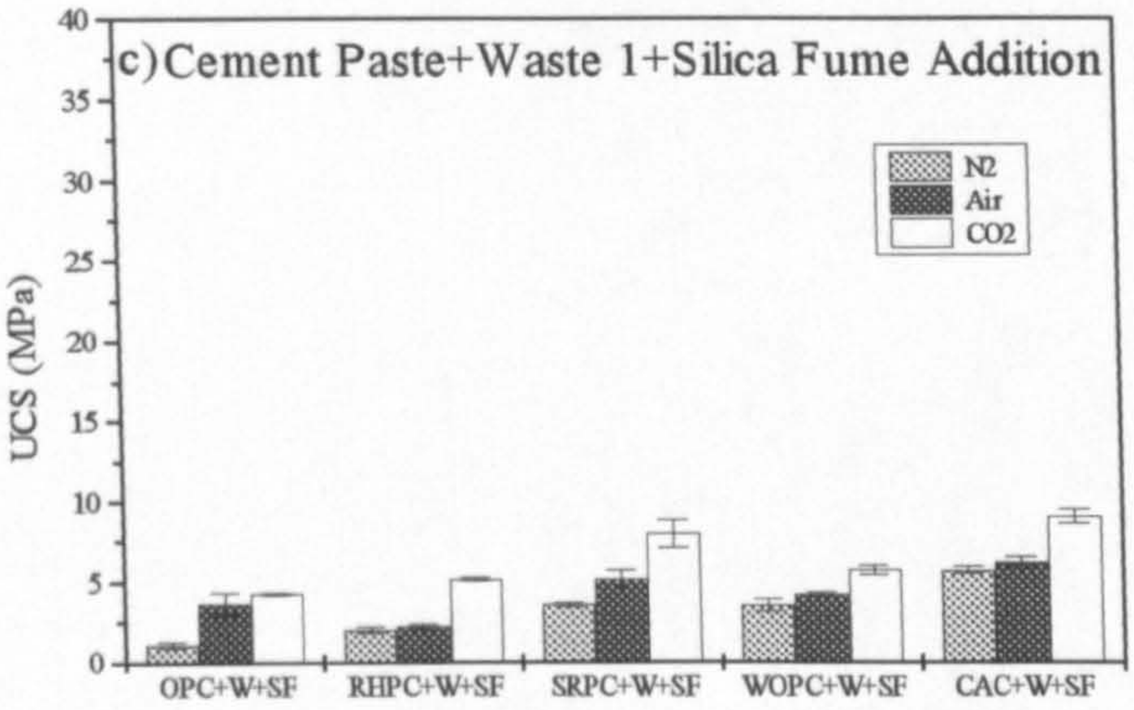
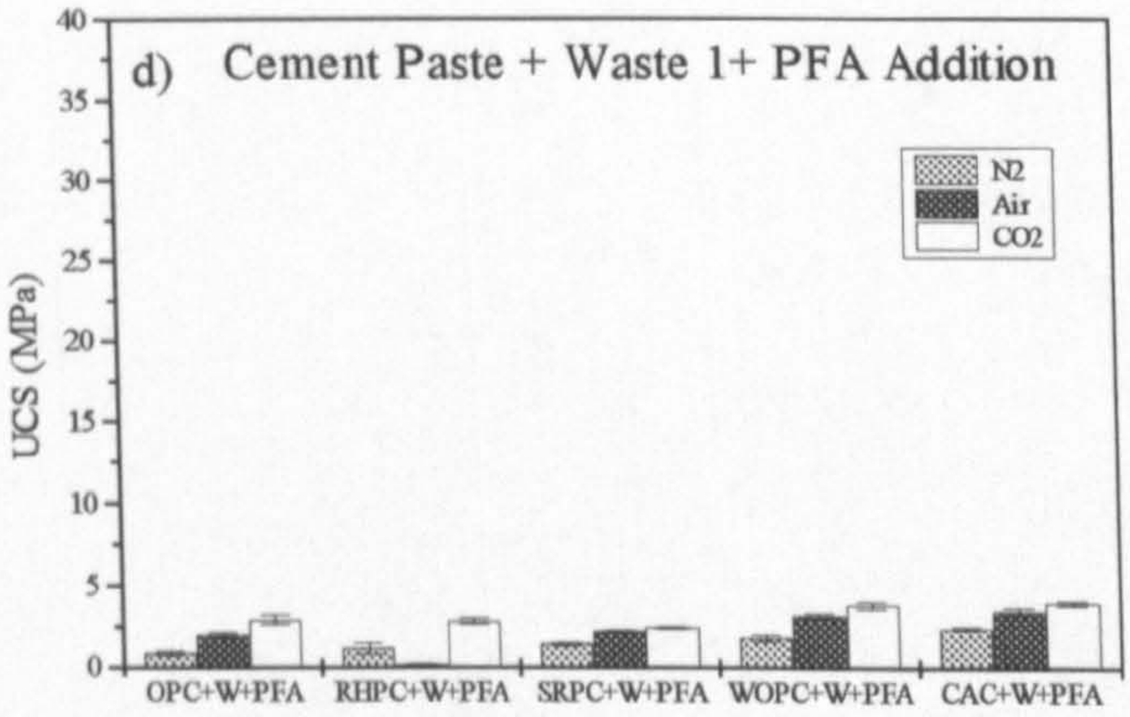


Figure 4.1a-b: Strength results after 28 days - control and cement paste/waste 1





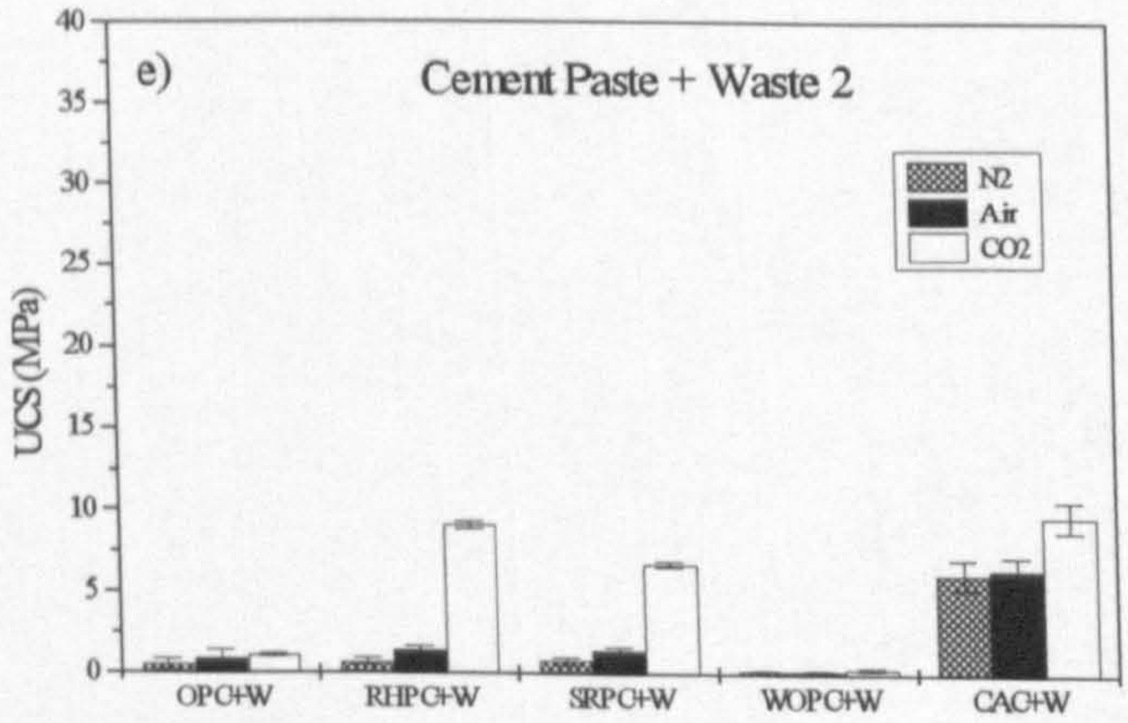
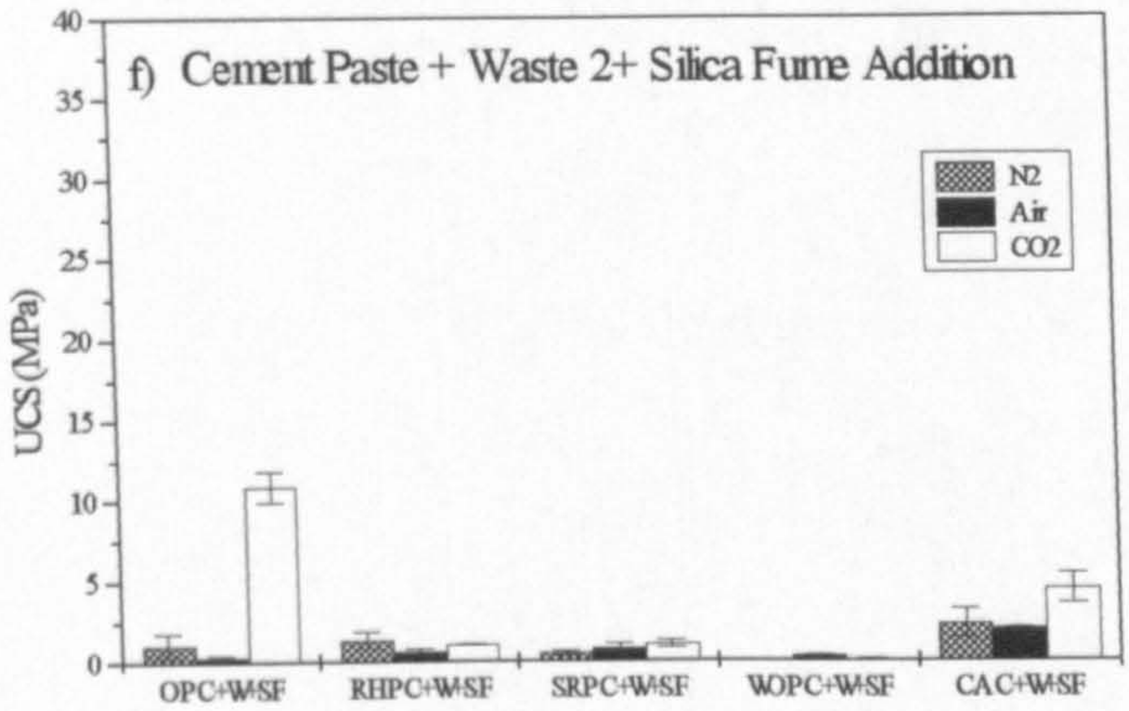


Figure 4.1c-e: Strength results after 28 days - c-d) Cement paste/waste 1/admixtures and e) cement paste/waste 2



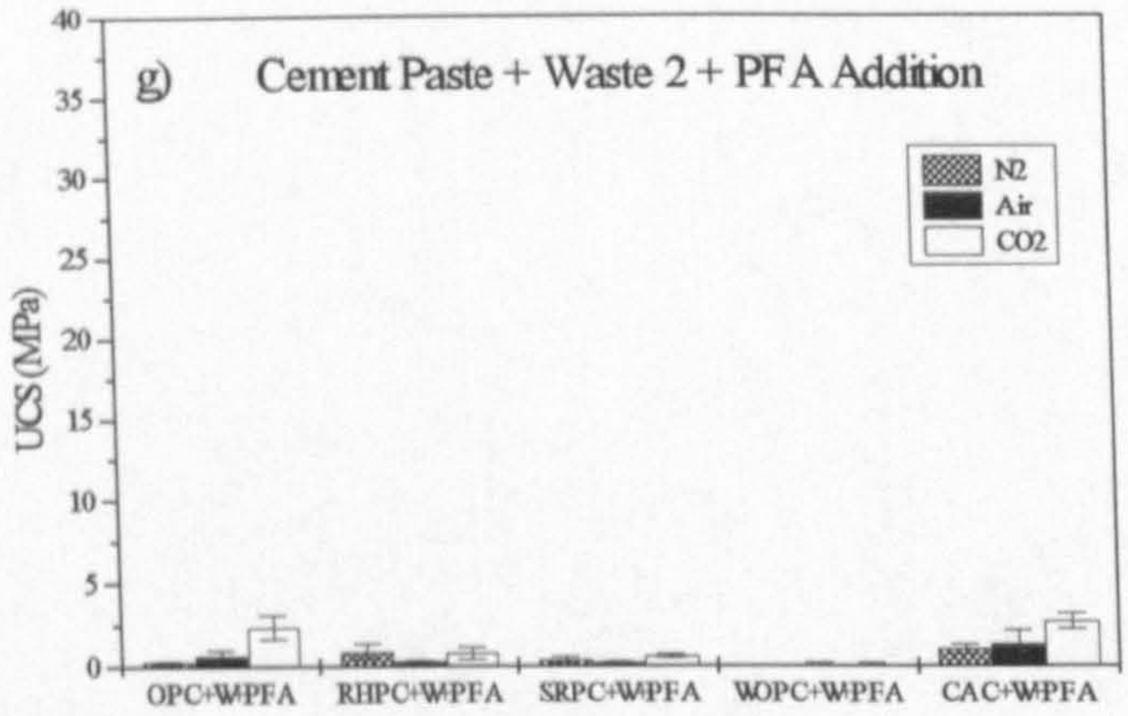


Figure 4.1f-g: Strength results after 28 days - cement paste/waste 2/admixtures

4.4.2 Phase Development

The phase development within the binder/waste samples is characteristic and may be seen by a comparison of the principal diffraction lines for each set of samples. In every case, a control chart was obtained using pure cement (waste-free) and the background intensities recorded were similar for all samples. Table 4.2 shows the intensity of qualitative x-rays for all mix designs. The x-rays diffraction patterns are shown in Appendix B with a summary of the x-ray data of the main crystalline phases for the raw wastes and their solidified products. The waste is largely an amorphous material and the crystalline components are various hydrates of calcium sulphate, calcite and portlandite.

Table 4.2: Intensity of qualitative x-Rays, in cp/s, recorded for waste forms solidified with different hydraulic binders

Waste 1 or Cory waste Specimens

Phase Dev.	Atm. Exposure	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	CO_2	165	283	318	338	131	437	236	249	228	175	197	301	275	117	110
Calcite	Air	118	127	102	116	74	126	128	130	89	80	93	83	88	61	82
	N_2	88	68	74	78	61	77	84	69	77	78	66	98	85	75	82
	CO_2	25	10	3	7	nd	2	15	18	nd	nd	12	nd	nd	34	nd
Portlandite	Air	23	nd	20	22	nd	24	22	17	17	nd	25	47	12	59	nd
	N_2	33	33	29	56	nd	36	28	37	38	nd	40	29	38	48	nd
	CO_2	42	30	30	32	nd	71	23	30	37	nd	35	22	31	31	nd
C_3S	Air	40	44	44	43	nd	32	30	39	39	nd	20	53	28	40	nd
	N_2	41	34	38	37	nd	46	39	40	41	nd	41	40	56	83	nd
	CO_2	21	39	72	64	nd	99	111	52	59	nd	60	48	48	36	nd
Gypsum	Air	105	135	155	91	nd	286	271	178	127	nd	117	120	194	34	nd
	N_2	12	34	37	22	nd	16	25	32	17	nd	19	22	25	64	nd
	CO_2	101	44	5	10	nd	nd	na	10	8	nd	na	20	48	20	nd
Ettringite	Air	43	50	42	59	nd	53	na	44	46	nd	41	71	63	110	nd
	N_2	134	127	119	132	nd	111	138	141	182	nd	132	127	185	179	nd

Waste 2 or Metal Colours waste Specimens

Phase Dev.	Atm. Exposure	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	CO_2	245	210	165	169	196	207	100	57	128	176	151	93	65	92	130
Calcite	Air	133	69	71	125	50	137	105	85	116	46	86	70	74	96	39
	N_2	81	66	46	100	nd	90	67	103	101	nd	67	65	48	142	nd
	CO_2	nd	nd	nd	nd	nd	10	nd	22	nd	nd	nd	nd	nd	21	nd
Portlandite	Air	19	nd	nd	nd	nd	nd	nd	nd	18	nd	nd	nd	24	nd	nd
	N_2	22	26	nd	nd	nd	24	nd	nd	nd	nd	30	nd	nd	nd	nd
	CO_2	57	20	22	78	nd	nd	38	52	91	nd	nd	30	20	87	nd
C_3S	Air	91	113	72	134	nd	81	149	71	109	nd	70	47	51	91	nd
	N_2	97	71	61	110	nd	105	73	61	128	nd	73	58	69	84	nd
	CO_2	29	nd	34	27	nd	nd	19	18	16	nd	21	nd	16	nd	nd
Gypsum	Air	nd	nd	21	nd	nd	12	23	nd	19	nd	19	nd	nd	18	nd
	N_2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	CO_2	24	nd	23	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Ettringite	Air	53	39	38	nd	nd	nd	27	40	nd	nd	23	32	nd	nd	nd
	N_2	76	63	54	45	nd	nd	59	56	53	nd	64	59	46	30	nd

c) Control Specimens

Phase Dev.	Atm. Exposure	1	2	3	4	5
	CO_2	192	189	117	159	42
Calcite	Air	138	73	56	78	28
	N_2	67	45	20	48	nd
	CO_2	28	20	64	nd	nd
Portlandite	Air	98	161	134	166	nd
	N_2	162	152	151	205	nd
	CO_2	27	nd	63	72	nd
C_3S	Air	91	84	88	103	nd
	N_2	115	109	108	144	nd
	CO_2	16	nd	17	nd	nd
Gypsum	Air	nd	nd	nd	nd	nd
	N_2	nd	23	nd	nd	nd
	CO_2	22	33	27	27	nd
Ettringite	Air	28	28	21	25	nd
	N_2	45	40	32	31	nd

The mix designs for samples 1 to 15 are given in Table 4.1.

Portlandite, which is added during the pre-treatment phase (neutralisation) of the waste, can be seen in its diffractogram, as a peak at 28.7 2θ (d-spacing 3.11Å).

The influence of the carbon dioxide curing environment in modifying the hydration of OPC, SRPC, RHPC, WOPC and CAC is well demonstrated in Table 4.2. As might be expected, with all samples calcite content increased in the following sequence: CO_2>air>N_2.

Ettringite appeared to decompose in the presence of carbon dioxide (as discussed previously) with a consequence increase in proportion of calcite and gypsum in the product. Aragonite and vaterite, which are a relatively unstable phases were not detected. Calcite, the most stable polymorph of $CaCO_3$, was the phase commonly detected at this stage.

4.4.3 Leaching Characteristics

Leachate metal concentration for all samples are given in Tables B.3 and B.4 (Appendix B). Figure 4.2 shows the concentrations determined for selected Cr, Cu, Zn and As. The pH values after 24-hour extraction procedure are recorded on Table 4.3. In general, the carbon dioxide-cured samples presented the lowest values for leachable metal for all mixes. Firstly, the benefits of using a carbon dioxide curing environment by comparison

with nitrogen/ambient conditions for solidified waste forms is shown by an improved metals fixation. Secondly, for different metals, a distinct binder-metal interaction appeared to occur, demonstrating that it may be advantageous to select cement binders depending on the metal content of the wastes. Also, the pH values of the samples cured in CO_2 indicated that carbonation has occured, lowering the pH by 3 to 4 units in comparison to nitrogen cured samples. Solidified wastes cured in normal (ambient) atmosphere showed a slight drop in pH, possibly as a result of the effects of atmospheric carbonation.

For W1, the addition of PFA and SF generally increased leachable metal concentrations for metals such as Cr by up to 20% when compared to cement /waste 1 mixes only. On the other hand, metals such as Ni, Zn and As showed much lower leachate concentrations when PFA was added. A reduction by up to 15% of leachable metal concentration for these metals was observed. For W2, a reduction of leachate concentration was observed when SRPC and WOPC were blended with SF/PFA for As.

The results outlined above indicate a significant improvement in both the physical and chemical properties of solidified waste forms when carbon dioxide was used as the curing environment. The carbonated solidified products in comparison with samples cured in nitrogen, were characterised by increased calcite contents of between 50% and 70%, increased strength of between 60% and 70% and a significant reduction in the leachable metal concentration by up to 80% for metals such as Zn, Ni, Cr and As.

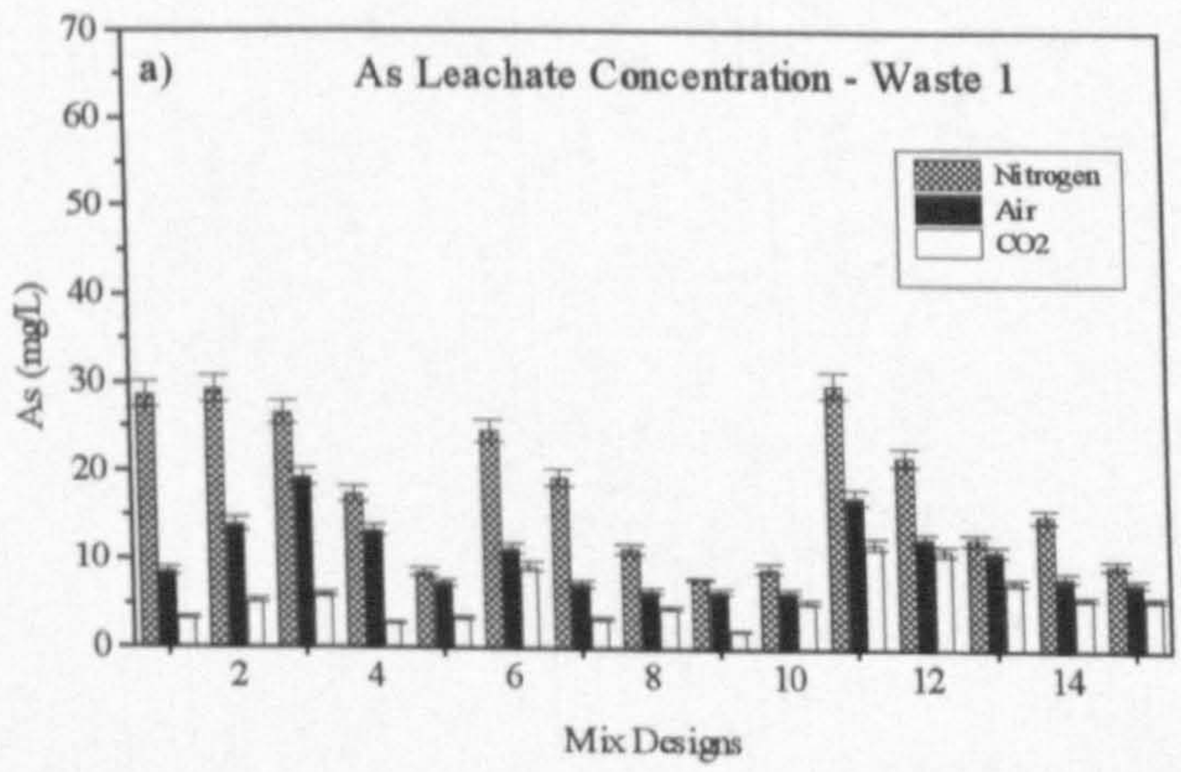
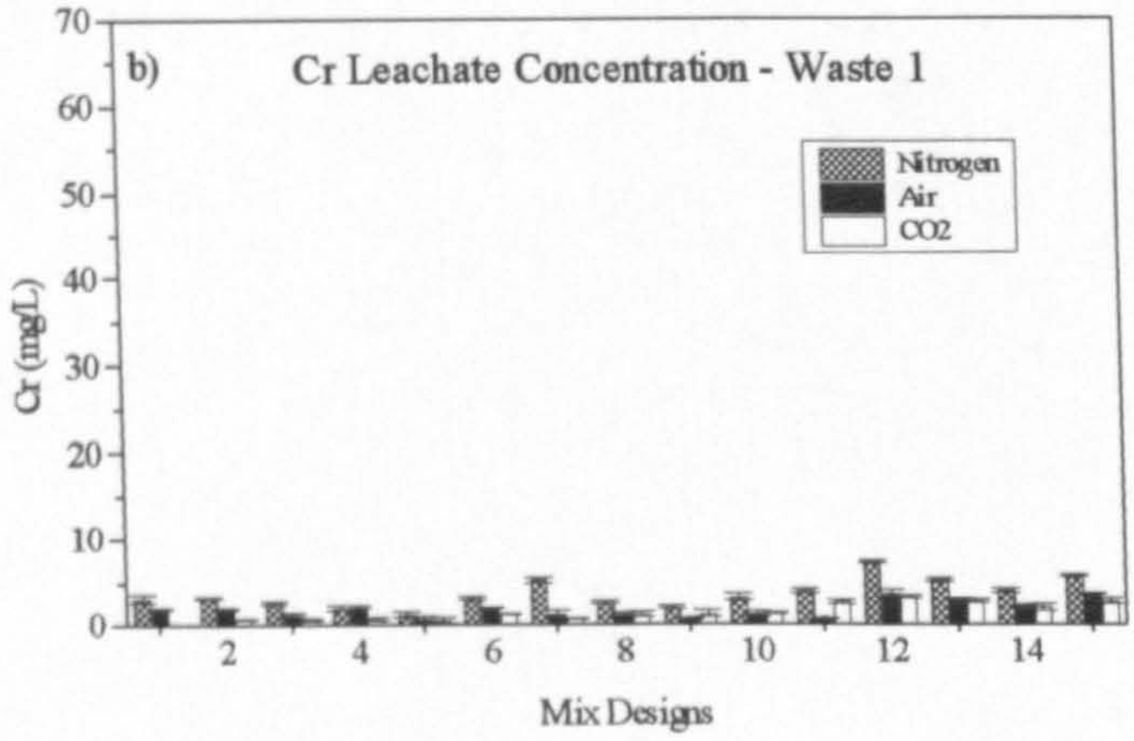
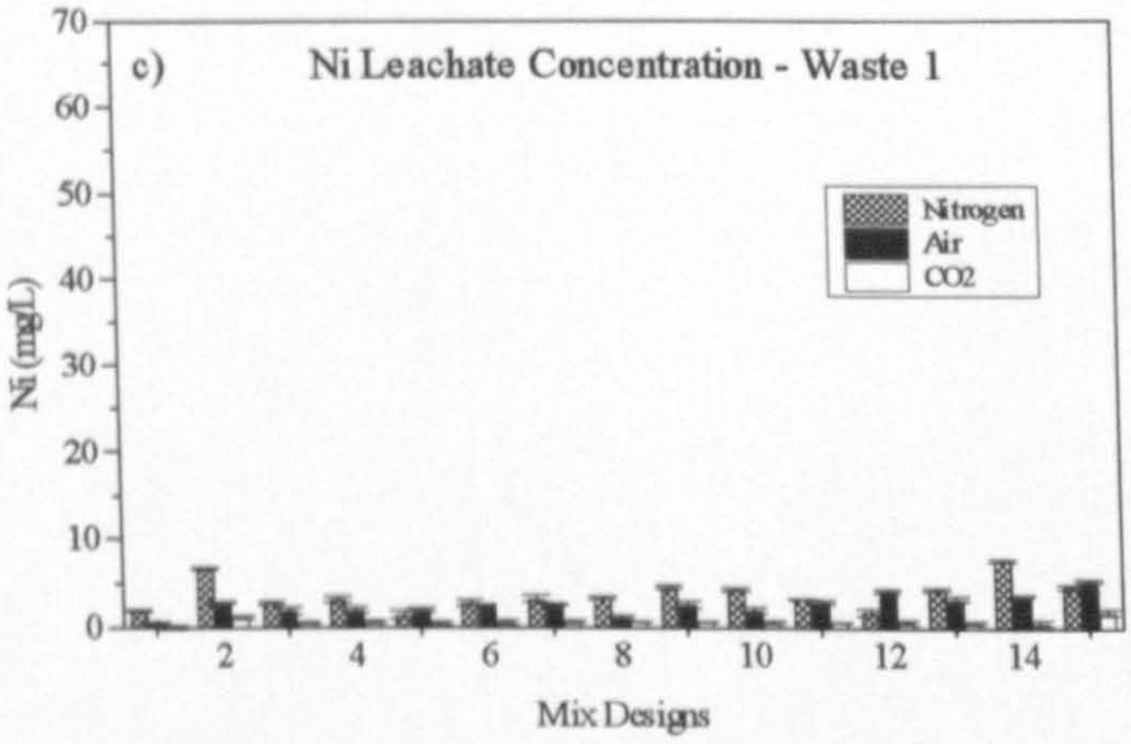


Figure 4.2a: Leachate metal concentration for As, Cr, Ni and Zn for different mix designs - As leachate concentration - waste 1





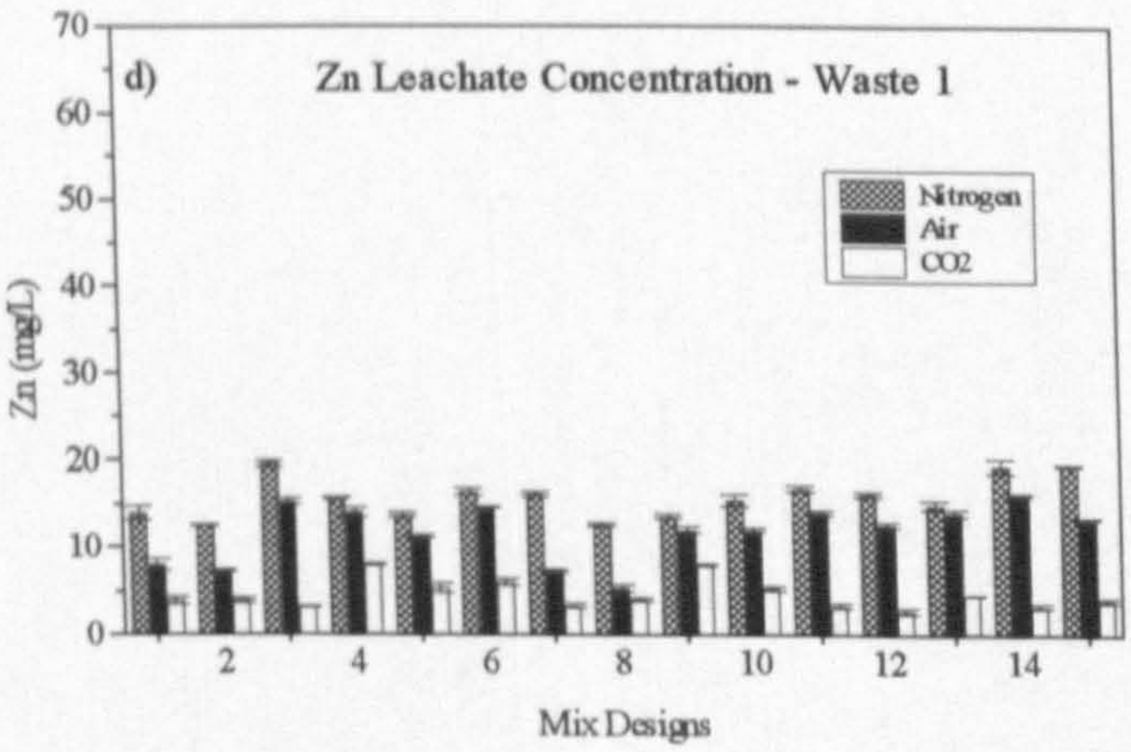
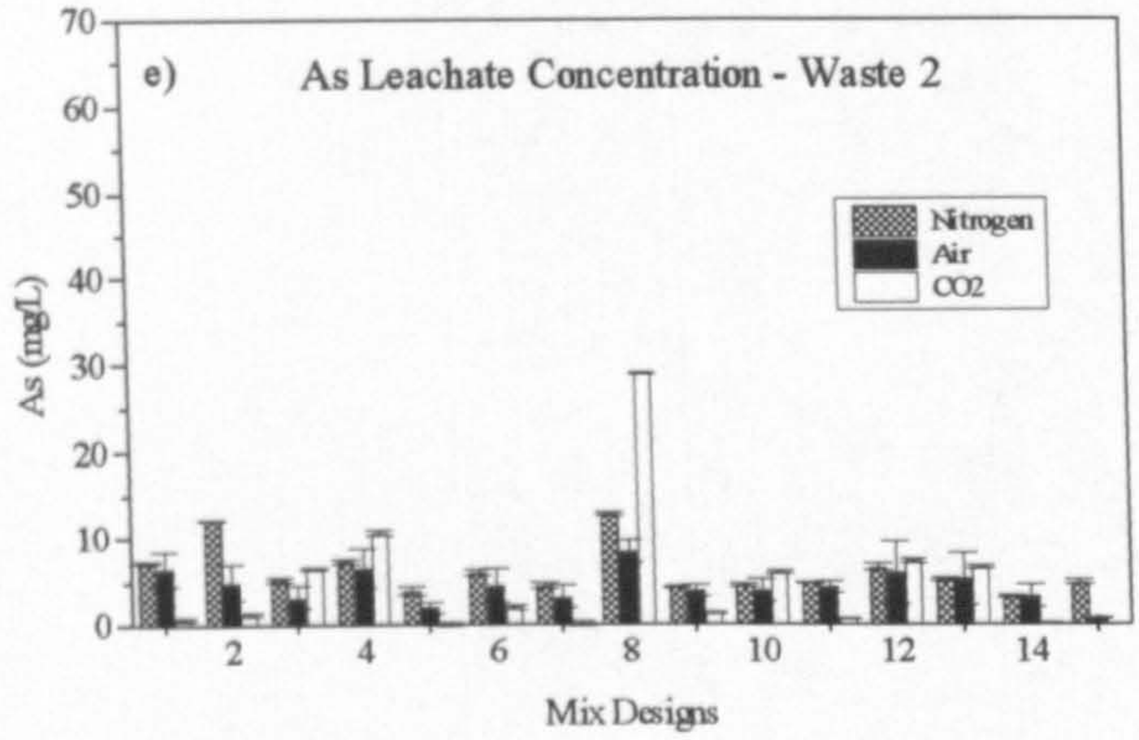
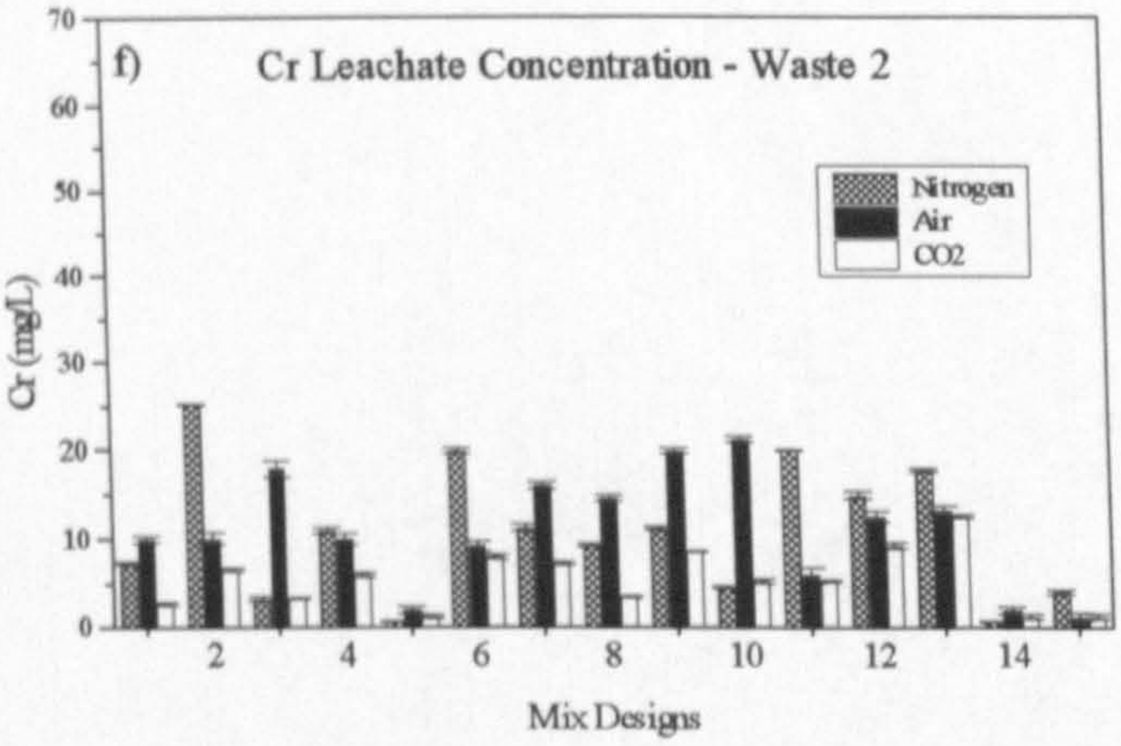


Figure 4.2b-d: Leachate metal concentration for As, Cr, Ni and Zn for different mix designs - c, d) Cr, Ni, Zn leachate concentration - waste 1





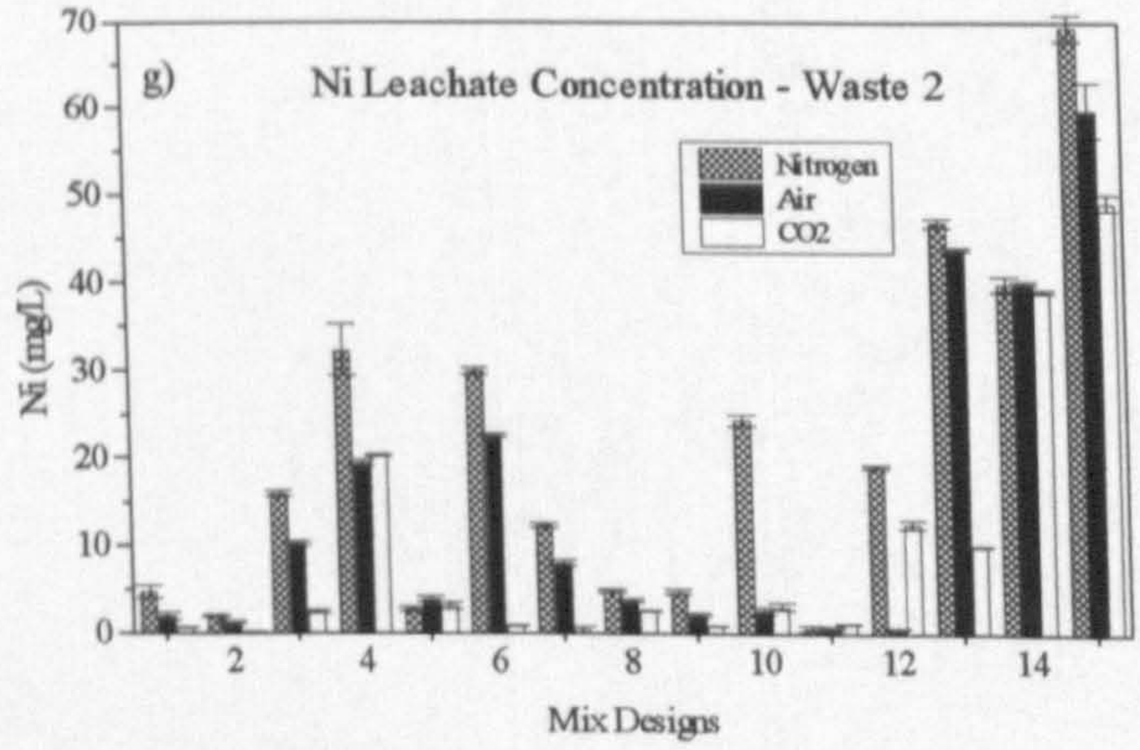


Figure 4.2e-g: Leachate metal concentration for As, Cr, Ni and Zn for different mix designs - As, Cr and Ni leachate concentration - waste 2

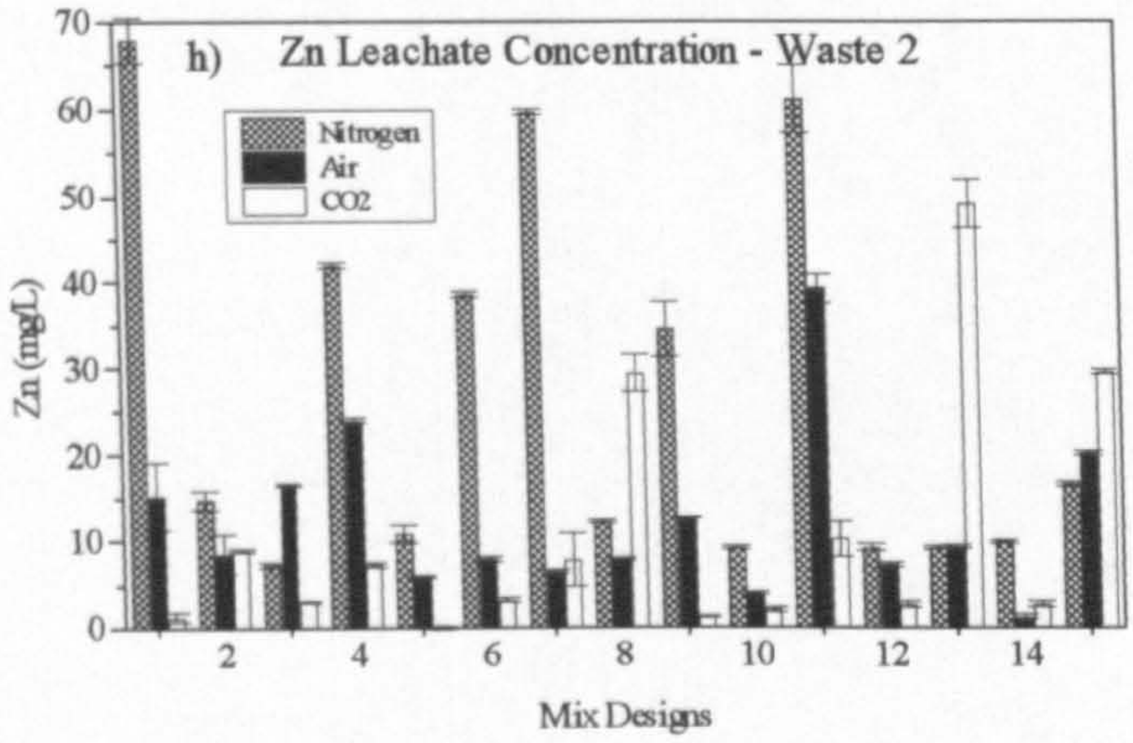


Figure 4.2h: Leachate metal concentration for As, Cr, Ni and Zn for different mix designs - Zn leachate concentration - Waste 2

Table 4.3: pH of leachate after a 24-hour extraction

Mixes	CO_2		N_2		Air	
	W1	W2	W1	W2	W1	W2
1	10.90	10.81	11.43	11.40	11.40	11.40
2	10.60	10.34	11.44	11.41	11.40	11.39
3	8.74	9.86	11.43	11.37	11.55	11.16
4	8.66	8.34	11.44	11.34	11.46	10.92
5	8.30	8.42	11.00	11.19	10.57	11.24
6	7.92	8.32	11.31	11.22	11.35	10.83
7	7.88	8.97	11.30	11.20	10.93	11.12
8	9.48	10.72	11.30	11.37	11.35	11.09
9	8.22	8.39	11.31	11.34	10.92	10.72
10	10.67	9.75	11.41	11.31	11.27	10.90
11	9.25	10.82	11.32	11.41	10.80	11.07
12	8.13	8.12	11.46	11.32	11.45	11.02
13	7.87	8.69	11.35	11.31	11.21	10.55
14	8.90	8.60	10.99	11.34	10.37	10.35
15	8.10	8.22	10.87	11.20	10.06	10.43

4.5 DISCUSSION

The effects of carbonation on the properties of cement bound waste forms are distinct and are generally appears beneficial rather than deleterious as is the case with structural concrete. The principal advantages result from improved metal binding capacity and mechanical properties.

Carbonation has been seen to play an important role in the hydration and polymerisation of silicates (Mollah et al., 1993) and the fixation of toxic metals appears to be linked at least in part with the formation of calcite; the possible formation of solid solutions with a large number of cations (Smith et al., 1991) and/or by sorption into gel hydration products (Richardson et al., 1993). However, the reactions taking place during binder hydration are complex and are probably modified by the addition of waste-contained species. Consequently, it may be necessary to consider the influence of antagonistic and synergistic effects of complex mixtures, which can interfere with hydraulic and pozzolanic reactivity when choosing inappropriate binder systems.

The principal effects of carbonation on the properties of blended and non-blended cement solidified waste forms can be summarised below.

Portland Cements

The most obvious effect of carbonation upon waste forms was on strength development. All four Portland cement/waste samples showed an increase in strength when cured in carbon dioxide. This may be due to an acceleration of hydration of C_3S driven by the formation of calcium carbonate. Examination of waste forms by x-ray diffraction showed that is possible to observe a strong relationship between C_3S hydration and the formation of calcite.

RHPC gave the highest strength values of all the Portland cements examined. This high-early-strength cement is more finely ground and has a slightly higher C_3A content. The hydration of C_3A forms ettringite, that may promote higher initial strength, however,

decomposition in the presence of CO_2 to form calcite among other compounds, may improve subsequent structural stability.

The phase development of waste forms may be primarily dependant upon both the curing environment and binder type. Ettringite, which is discussed above, clearly is decomposed to form alumina-gel, gypsum and calcite. Calcite was also found in abundance in C_3S-rich binders, such as RHPC and WOPC.

A significant difference was found between the levels of leachable metals in samples cured in CO_2 and N_2. The drop in leachate pH values after 24-hour extraction, on samples cured under CO2 atmosphere, showed that not only carbonation had occurred, but also that certain metals such as Cr, Ni and Zn were retained in the waste forms.

The minimum solubility of $Cr(OH)_3$ is between pH 8.5-9.5, for $Zn(OH)_2$ at pH 9.2 and $Ni(OH)_2$ at pH 10.0 (Conner, 1990). On this basis it might be expected that a higher amount of Cr, Ni and Zn might be released as pH drops as result of carbonation to typically between pH 8.0 to 8.5. As this was not observed it indicates that physical containment of these metals was enhanced, by for example, the formation of calcite, modifying pore structure and the precipitation of double salts containing these species. However, in saying this, direct evidence of the latter was not obtained from an analysis of waste form x-ray diffractograms, although some unidentified peaks were apparent.

The modification of C-S-H, previously discussed (Smith et al., 1991), where a C-S-H-CO_2 reaction can compete and compliment the CH-CO_2 reaction leading to a siliceous product characterised by a degree of polymerisation higher than the original C-S-H; and which may 'capture' certain metals. In the literature (Mollah et al., 1992b), presented evidence to suggest that some metals, such as zinc, may enhance carbonate formation through the precipitation of $CaZn_2(OH)_6.2H_2O$, which can prevent the formation of a tobermorite structure and 'liberate' $Ca(OH)_2$ normally bound between two octahedral silicate sheets. Consequently, $Ca(OH)_2$ will be more accessible to carbon dioxide for carbonate formation.

Calcium Aluminate Cement

When CAC was used to solidify the waste, strength values up to 35% higher than OPC were obtained despite the presence of waste.

Examination by x-ray diffraction indicated the presence of calcium carbonate in the solid phase. The formation of calcite indicates the presence of free lime which may not have been anticipated but which was most likely facilitated by the presence of alkali carbonates from the waste and by a reaction with the hydrated calcium aluminates (Eq. 4.4). The alkali carbonate thus acts as catalyst in the modification of calcium aluminates to form calcite.

Leachate analysis showed a significant reduction in extractable metal concentration for samples exposed to a carbon dioxide environment. Again, changes in the pore structure due to the presence of calcite and a possible incorporation of some metals by AH_3 gel could explain this phenomenon.

Pozzolanic Additives

Mineral admixtures may significantly affect the size, distribution, structure and composition of cement paste hydrates. Typically on addition of PFA and SF to cement less CH is liberated and the Ca/Si ratio in C-S-H is lowered (Atkins et al., 1989; Mehta, 1989; Roy, 1989). SF particles typically fill the void space between cement grains and a pozzolanic reaction takes place with portlandite. For PFA, as a consequence of the breaking down of the alumina-silica glass structure, the content of aluminium, potassium and sodium in C-S-H increases and reaction products derivated from the hydration and carbonation itself tend to precipitate within the small pores (hydration products, carbonated species, etc.) (Fraay et al., 1989).

In this study, cement/waste samples blended with PFA showed a lower 28 day strength when compared with samples blended with SF. This is explained as being due to initial retardation by precipitation of hydration reaction products of cement on the PFA particles (Mehta, 1989).

The hydration reactions in cement/waste systems incorporating PFA and SF were responsible for changes in microstructure. A decrease in the amount of calcite was observed for samples cured in carbon dioxide when compared to cement only binder. The pozzolans remove CH from the binder, densify the paste and reduce gas permeability making it more difficult for CO_2 to diffuse into the paste.

From the leaching results it was clear that PFA and SF improved the metal fixation for some of binder systems, for example Cr in the WOPC/SF/W1 mix cured in carbon dioxide.

4.6 SUMMARY AND CONCLUSION

Properties of selected binders systems mixed with two commercially solidified wastes that were cured in carbon dioxide, air and nitrogen atmospheres have been investigated in this Chapter.

Samples cured in a carbon dioxide environment gave improved mechanical properties and increased toxic metal binding capacity, when compared to samples cured in nitrogen or normal atmospheric conditions. The carbonated solidified products had mean strength values increased by up to 70% and leachable metal concentrations reduced by up to 80% as against their non-carbonated analogues.

The type of binder used influences the degree of carbonation and the degree to which waste metals can be immobilised. Thus, the nature of the binder needs to be taken into account in order to maximise the effective solidification and fixation of the waste material within the carbonated waste form. For example, calcite formation was found to be more abundance in C_3S-rich binders.

The potential importance of the carbonation reaction has been seen in this part of the work. However, the precise mechanisms of metal fixation during carbonation and their effect on the nature of bonding of different waste species within hydrated carbonated cement-based systems have yet to be elucidated. One important aspect to be addressed is

to determine the quantity of carbon dioxide absorbed by the different binder/waste systems in order to allow correlation with the properties of the solidified product.

Thus, the following Chapter is concerned with the study the kinetics of the carbonation reaction, by investigating the effect of mix variables on the rate and extent of the carbonation.

CHAPTER 5

THE INFLUENCE OF MIX PARAMETERS ON THE KINETICS OF THE CARBONATION REACTION DURING THE SOLIDIFICATION OF HAZARDOUS WASTE

5.1 PREVIEW

In Chapter 4 the effects of carbonation upon the phase development and leaching properties of blended and non-blended cement-solidified waste products were investigated. Improved metal binding capacity was observed for carbonated samples, and the type of binder selected appeared to have a key role in determining the nature of the carbonation reaction. All the cements and mineral admixtures examined reacted with carbon dioxide, although calcium aluminate cement less so in comparison to Portland cements.

The purpose of this Chapter is to study the kinetics of the carbonation reaction under normal environment conditions, i.e., atmospheric pressure and room temperature. The process governing the diffusion of CO_2 into waste forms is discussed with reference to water/cement and waste/binder ratios for the different systems examined. The results for total uptake of CO_2 and/or rate of carbonation are obtained using a Eudiometer for the different waste/binder mixes and areas showing the degree of carbonation for each cement system are defined.

5.2 GENERAL BACKGROUND

Previous Chapters have demostrated that severe retardation of hydration seen in solidified waste products containing heavy metals can be overcome through acceleration of the hydration reaction of C_3S (Lange et al., 1996) due to carbonation. Carbonation has also been shown to improve the chemical and mechanical properties of blended and non-blended cement-solidifed materials (Lange et al., 1997).

When accelerated carbonation was applied to cement mortars, some authors observed that for different water/cement (w/c) ratios and compactions, significant strength values could be generated within minutes (Klemm et al., 1972; Young et al., 1974; Sorochkin et al., 1975). These result from the reaction of C_3S and β C_2S, which hydrate extensively, according to:

$$C_3S + yH_2O + (3\text{-}x)CO_2 \rightarrow C_xSH_y + (3\text{-}x)\,CaCO_3 \qquad \text{(Eq. 5.1)}$$

or

$$+ zCO_2 \rightarrow C_{(x\text{-}z)}SH_y + zCaCO_3 \qquad \text{(Eq. 5.2)}$$

In reality, Sorochkin et al. (1975) have better demonstrated the dependence of the strength of specimens on the forming pressure and this relationship is further examined in this work for OPC/sand samples, and illustrated in Figure 5.1. It is seen that at each water/cement ratio the grains in a mixture of any w/c ratio are brought together to the optimal distance for access of CO_2 to then only under a particular compressive force.

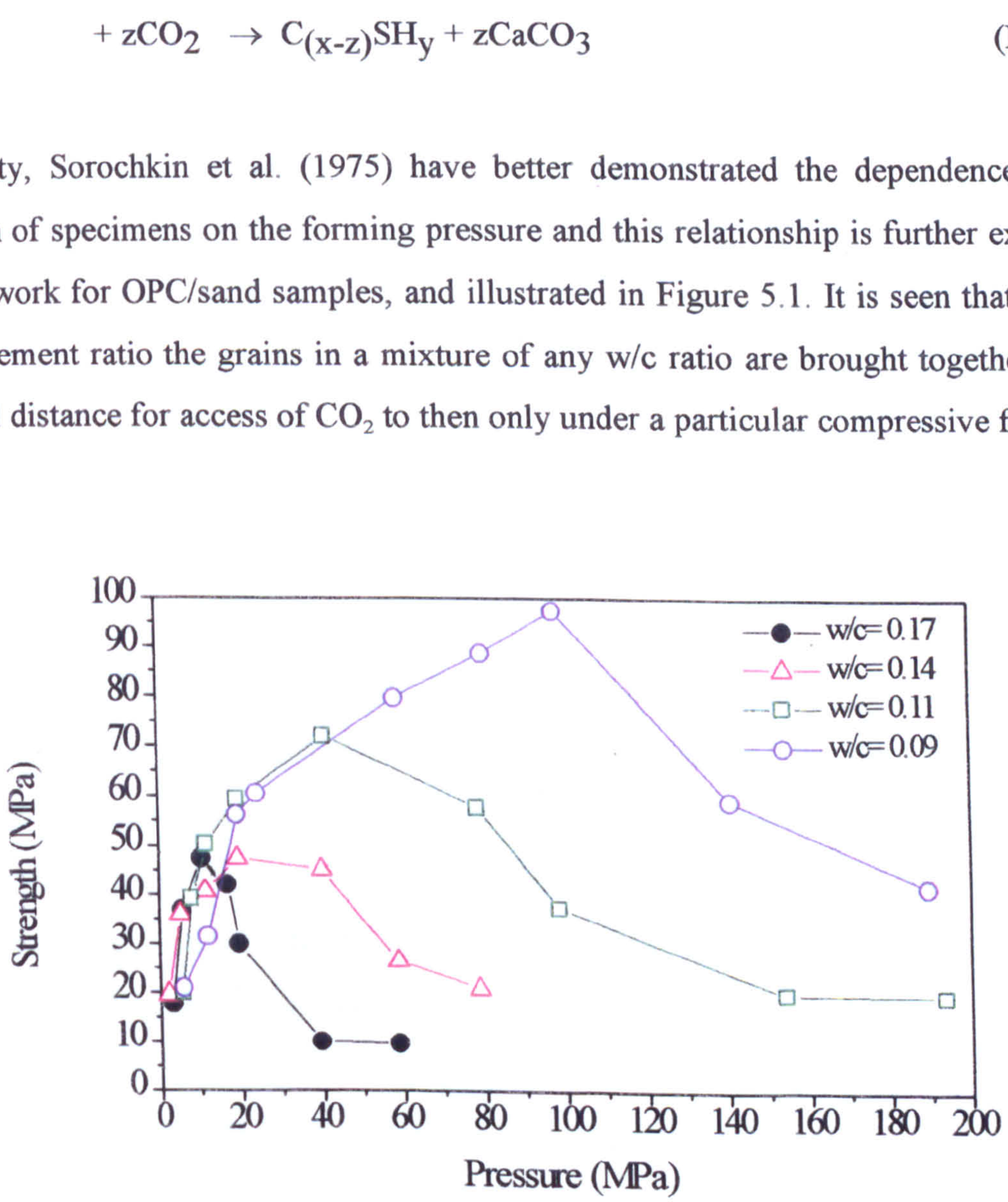


Figure 5.1: Dependence of strength of carbonated OPC/sand samples at various w/c ratios on the forming pressure

It was also suggested that the rate of carbonation would be limited by diffusion, and thus the rate of hardening in a carbon dioxide atmosphere would be dependent on penetration of carbon dioxide into the material. In practice, carbonation is a complex process and very much dependent on the nature of the type of cement as well as the porosity, permeability and w/c ratio (Calleja, 1980; Parrott, 1992; Saetta et al., 1993). The environmental conditions, such as humidity and carbon dioxide pressure also have important effects on the setting and curing process (Fattuhi, 1988; Reardon et al., 1989).

The aim of the work described in this section is to study the kinetics of the carbonation reaction under normal environmental conditions (atmospheric pressure and room temperature) during solidification of the two industrial wastes previously investigated. Portland cement-based materials have shown to be more reactive to the presence of carbon dioxide than calcium aluminate cements in a short term. Therefore, Ordinary Portland cement (OPC), white Portland cement (WOPC) and sulphate resisting cement (SRPC), blended and non-blended are the cements subjected to investigation here.

5.3 MATERIALS AND EXPERIMENTAL METHODS

The materials (OPC, WOPC, SRPC, PFA, GGBS, Cory waste - W1, and Metal Colours waste - W2) and the method of recording CO_2 consumption were described in detail in Chapter 2. Control (waste-free) mixes were also prepared using the same binders and a fine inert sand (<500 μm) to replace the waste. A wide range of mixes were used to prepare samples in triplicate and the addition rate for the different compounds are given in Table 5.1. Figure 5.2 shows the mix designs chosen.

After mixing, samples were submitted to a standard compaction pressure of 1 MPa using a hydraulic press. Here 1 MPa was chosen as a standard compaction pressure as question of practicality. However, for samples with w/c ratio higher than 0.4 this standard compaction was not applied to avoid the evolution of bleed water.

Table 5.1: Addition rates of the materials used

Materials	Δ Addition Rate - %(w/w)
OPC	10 - 90
WOPC	10 - 90
SRPC	10 - 90
PFA	15
GGBS	40
Waste 1	10 - 80
Waste 2	10 - 80
water/binder (w/b) ratio	0.07 - 3.0

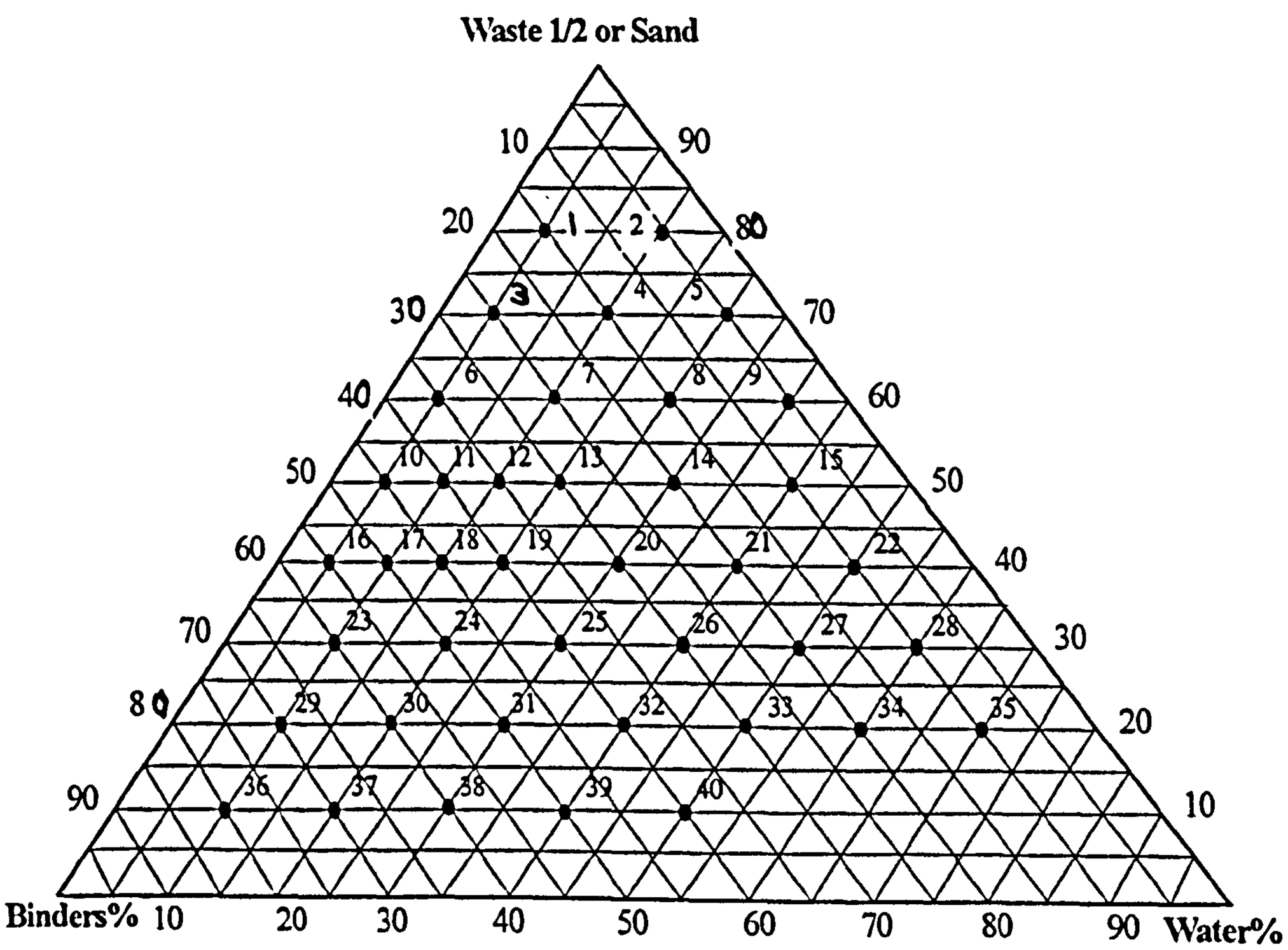


Figure 5.2: Ternary diagram showing the mix designs investigated in this work

Immediately after preparation the samples were placed in the Eudiometer and the experiment conducted as described in Chapter 2. Samples with very high w/c ratio were constantly agitated during carbonation to avoid sedimentation of material at the bottom of the sample holder. Every 10th sample consisted of a control sample to ensure the reproducibility of the method. The samples were analysed in triplicate and a 95% confidence interval was determined to estimate the range within which the true mean may be found.

5.4 RESULTS

Figure 5.3 shows eudiometer traces for 3 mixes consisting of OPC, WOPC and SRPC and waste 1, at two different w/c ratios. Appendix C gives the Eudiometer results for all samples. It can be seen that during the first 15 minutes, the carbonation reaction was extremely rapid, and that the induction time (the interval between mixing and the start of the reaction) was extended at higher w/c ratios. OPC appeared to react more quickly with CO_2 at the lower w/c ratio than WOPC and SRPC.

From the measurements of total carbon dioxide uptake for the different mix designs (Figure 5.2), it was possible to define three distinct fields related to the degree of carbonation of the samples and they are illustrated in Figure 5.4a-g. They are nominated as: H= highly carbonated; M= moderately carbonated and P= poorly carbonated. All results in % CO_2/w/w solids.

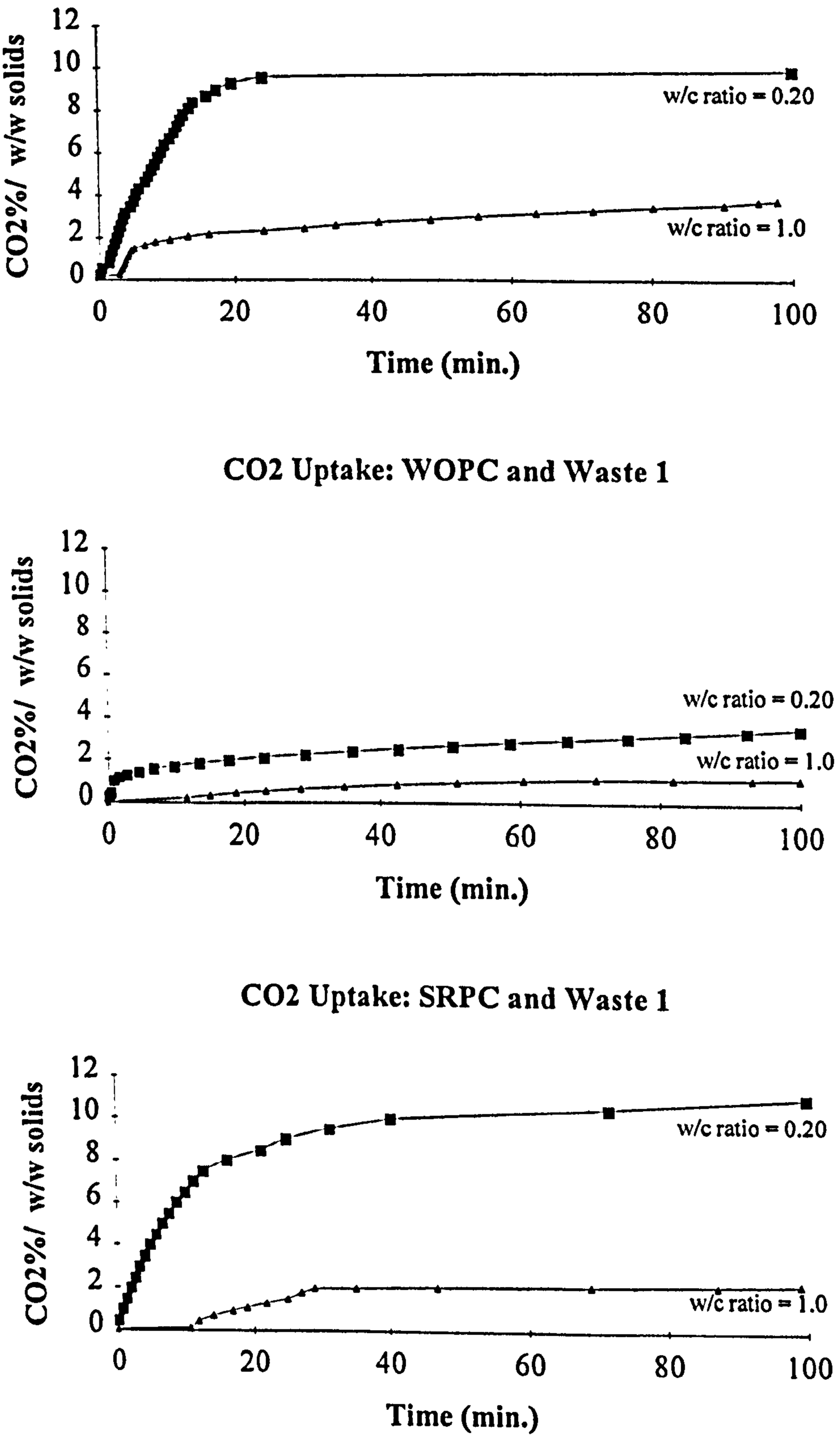
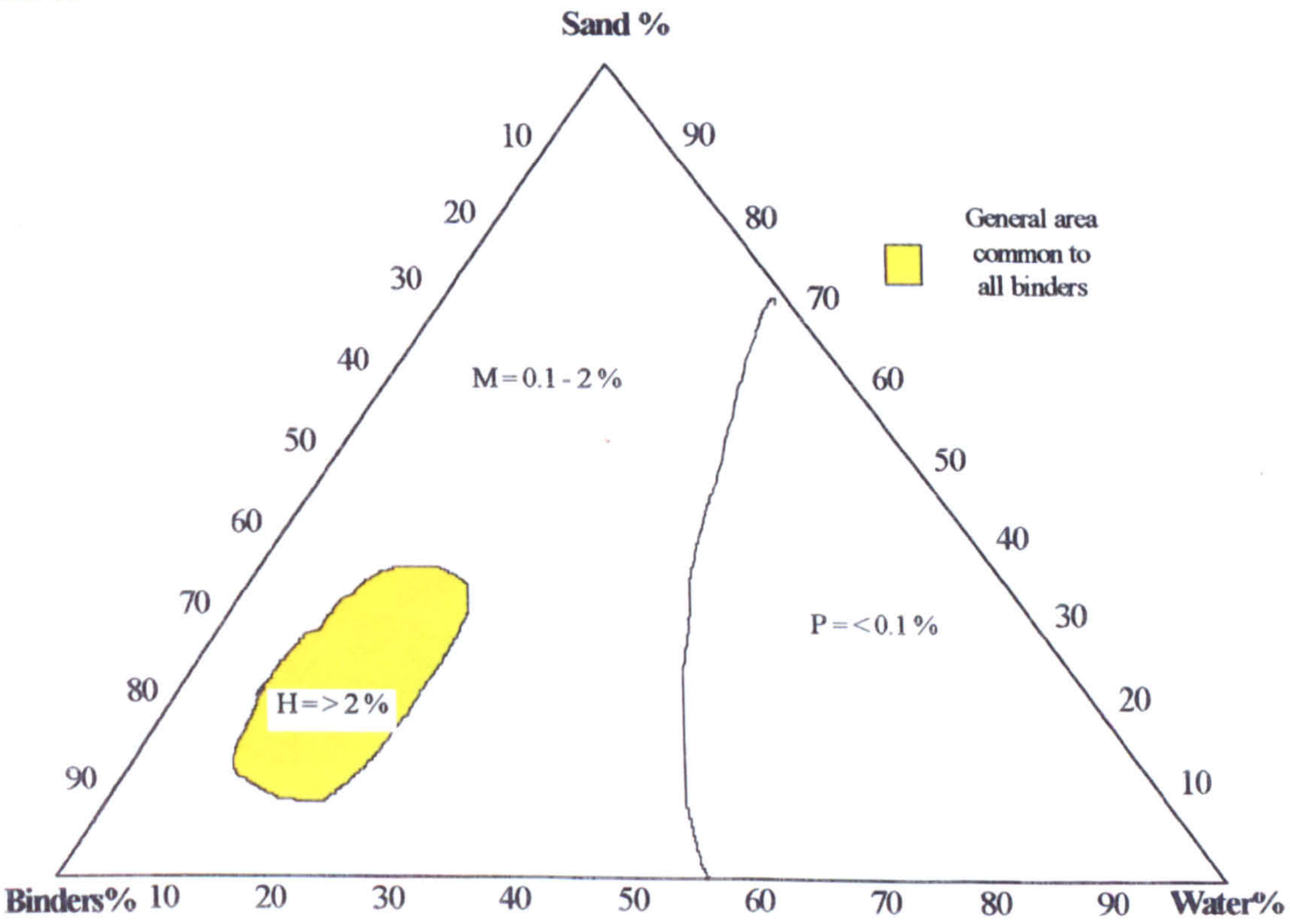


Figure 5.3: Rate of CO_2 consumption for mixes at w/c of 0.2 and 1.0

a) Control



b) OPC/ admixtures/Waste 1

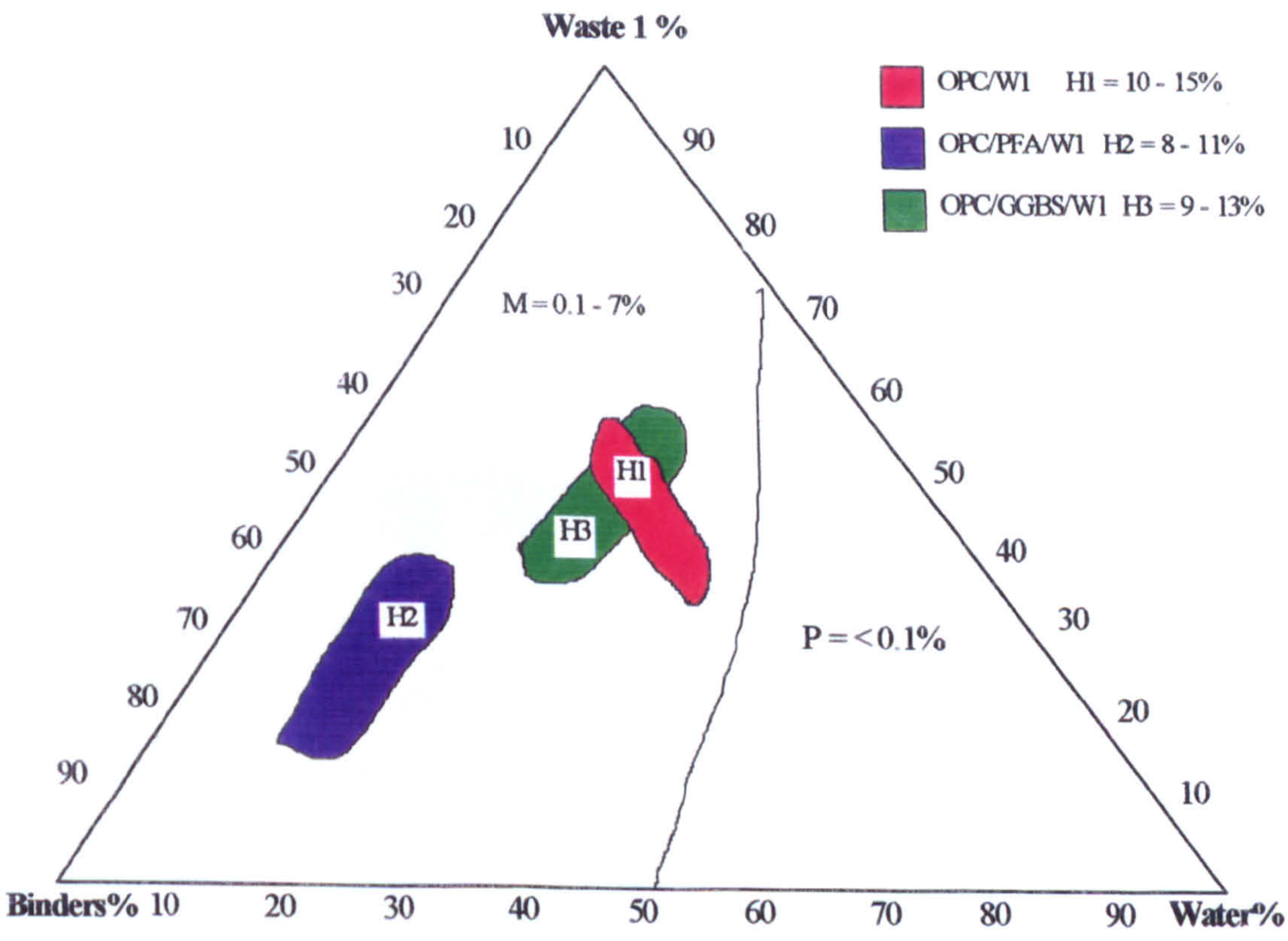
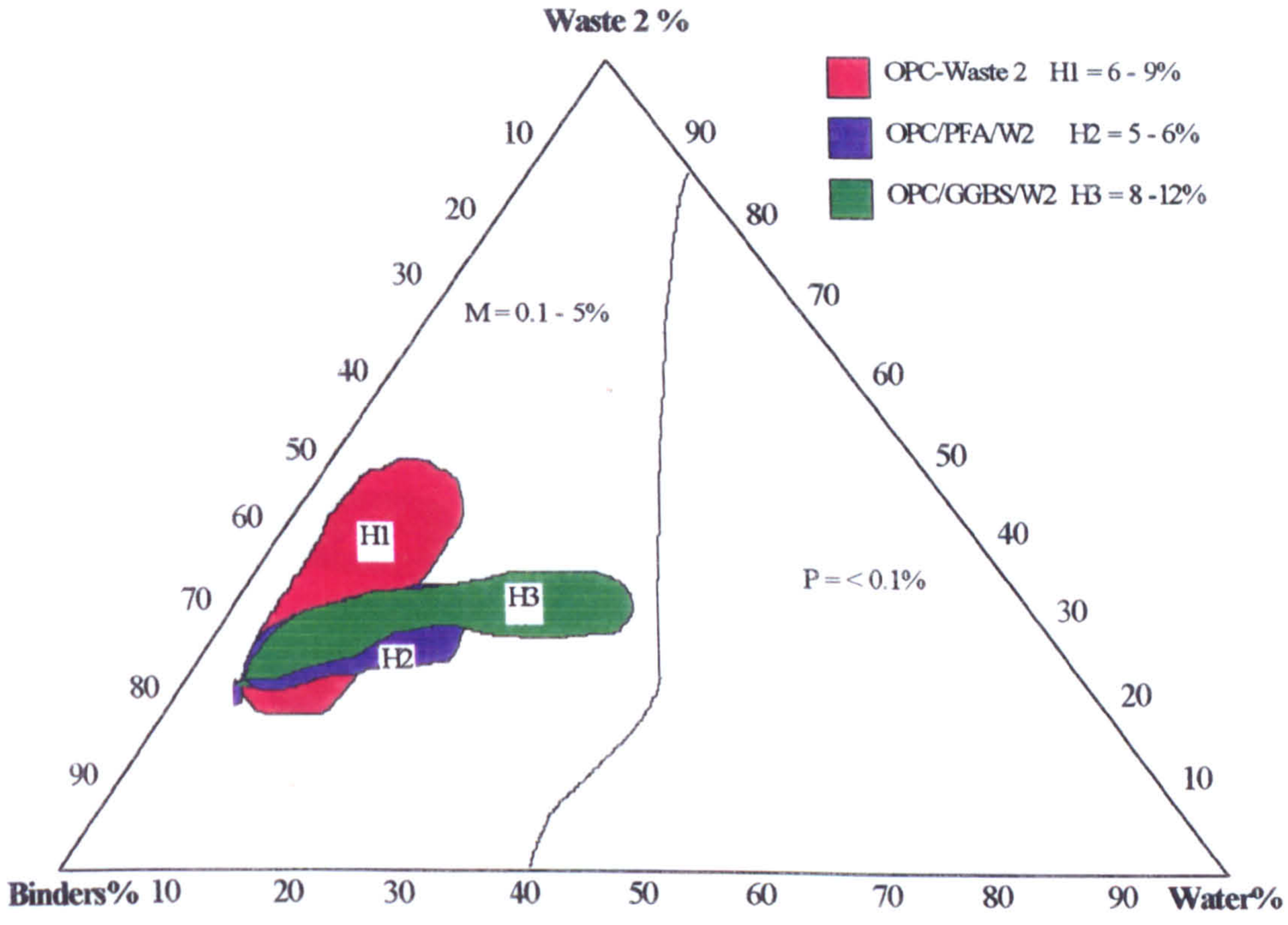


Figure 5.4a - b: Ternary diagrams for the different waste/binder systems showing the effect of mix proportions on the degree of carbonation

c) OPC/admixtures/Waste 2



d) WOPC/admixtures/Waste 1

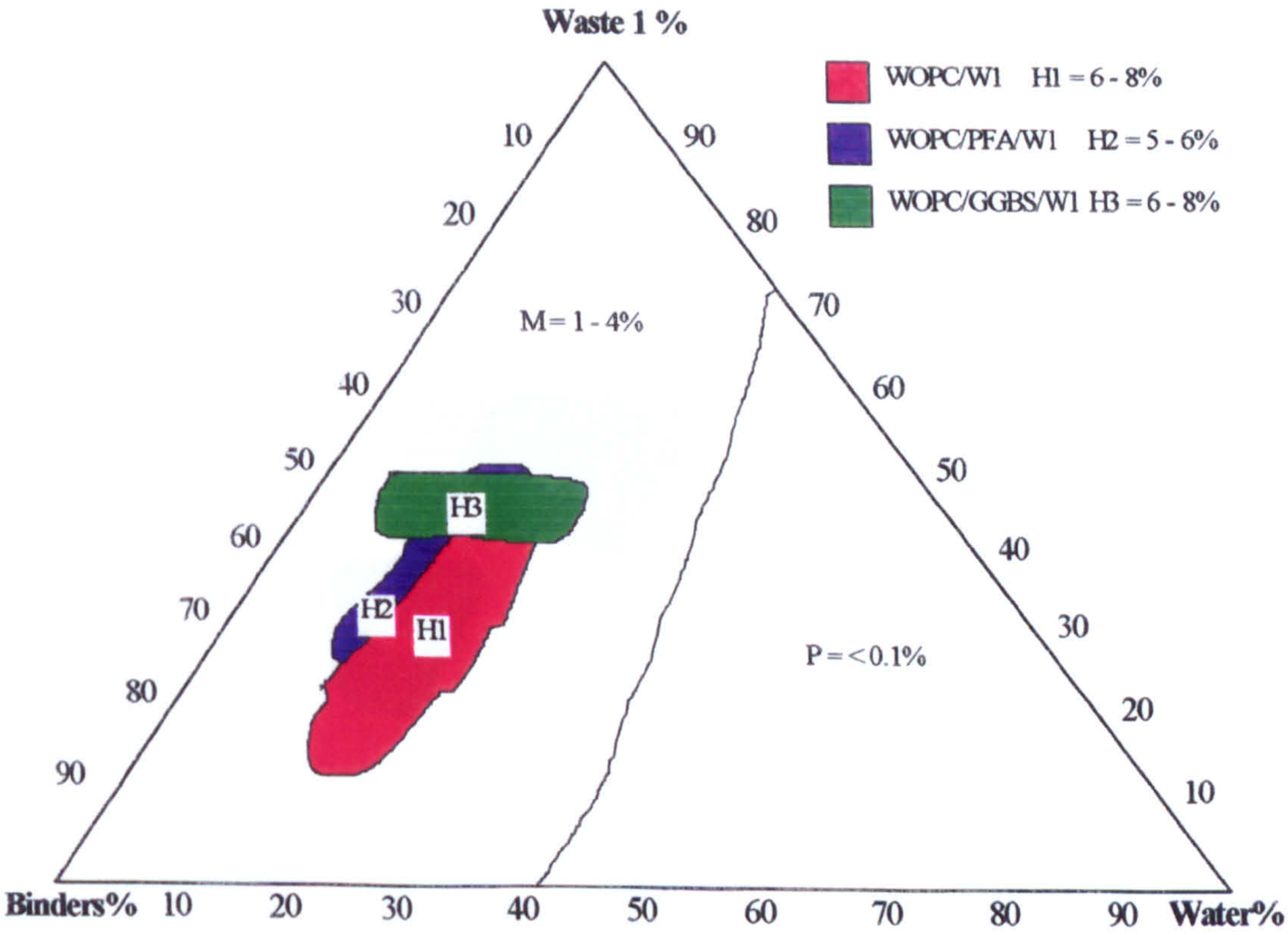
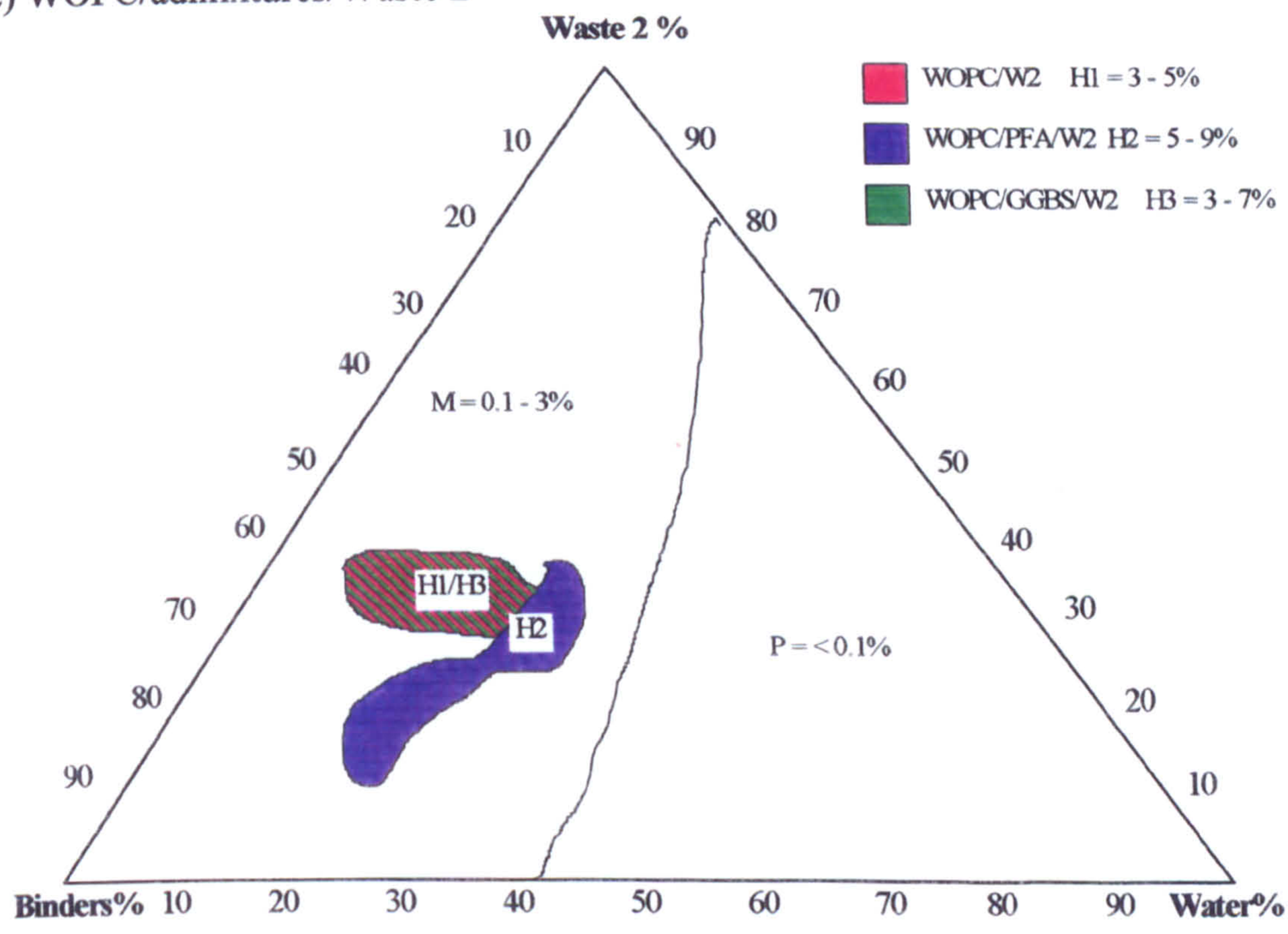


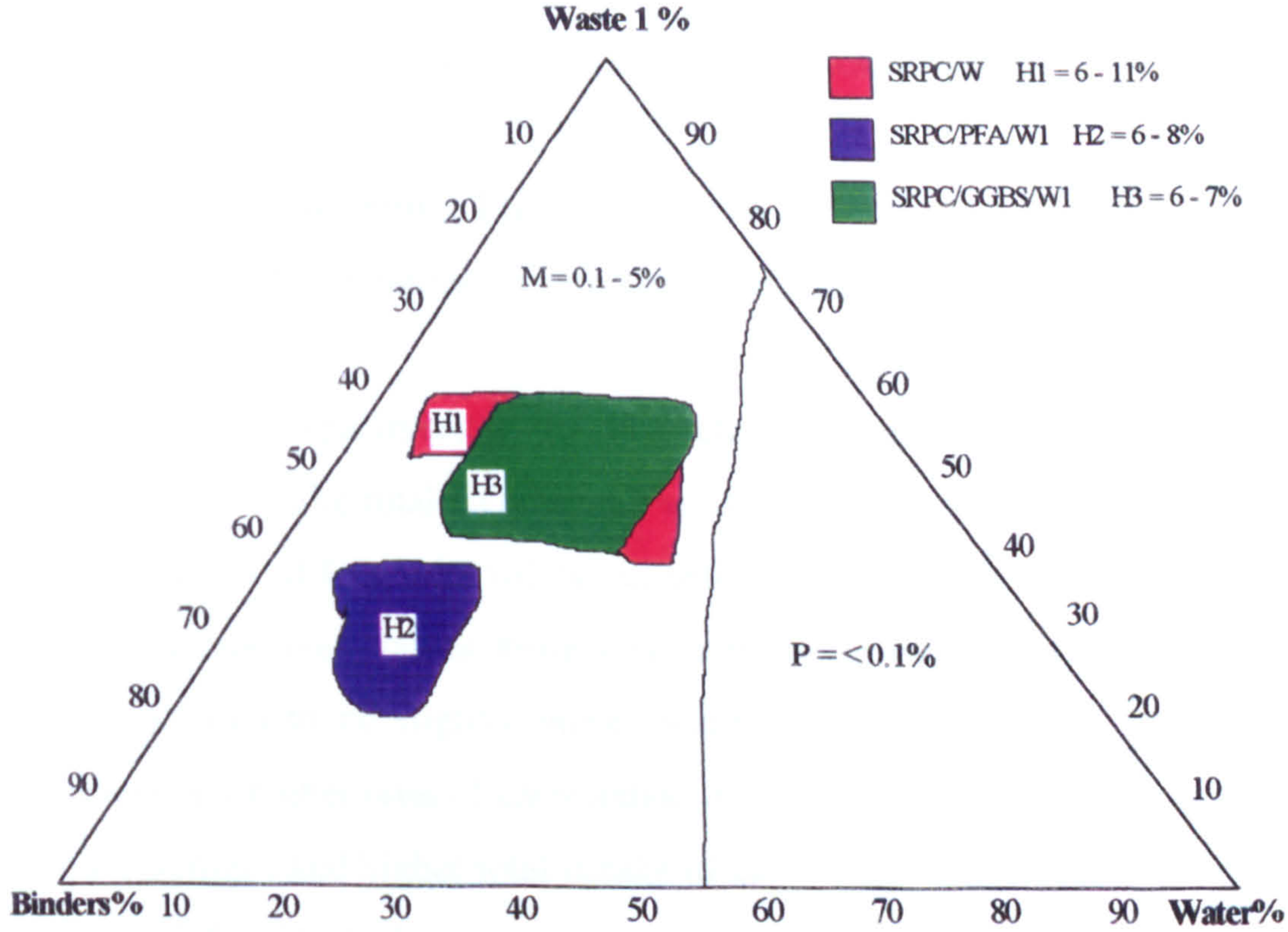
Figure 5.4c - d: Ternary diagrams for the different waste/binder systems showing the effect of mix proportions on the degree of carbonation

e) WOPC/admixtures/Waste 2



Note: The area of WOPC/GGBS is overlapped by WOPC only

f) SRPC/admixtures/Waste1



Note: The SRPC only area is partially overlapped by SRPC/GGBS

Figure 5.4e - f: Ternary diagrams for the different waste/binder systems showing the effect of mix proportions on the degree of carbonation

g) SRPC/admixtures/Waste 2

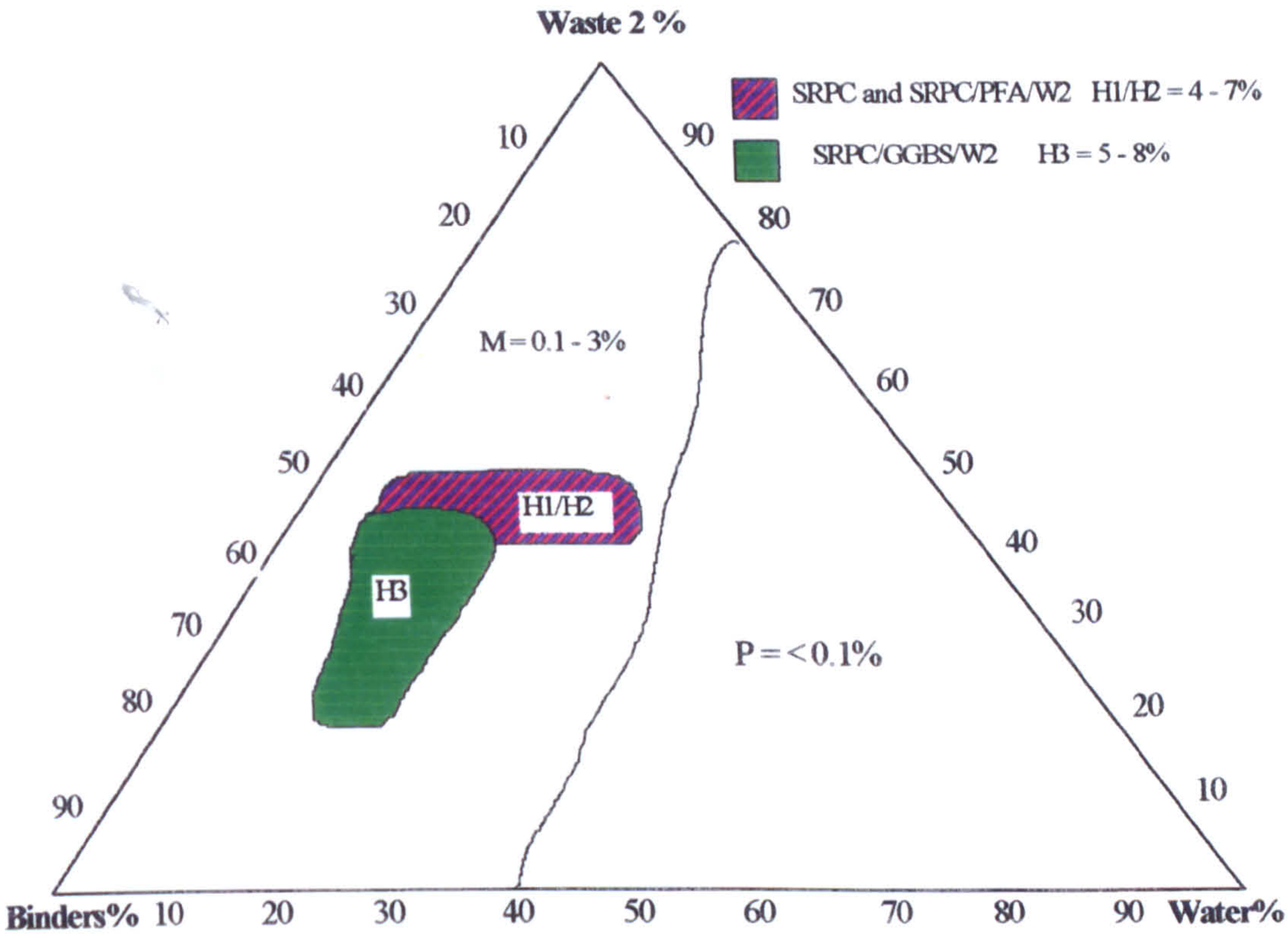
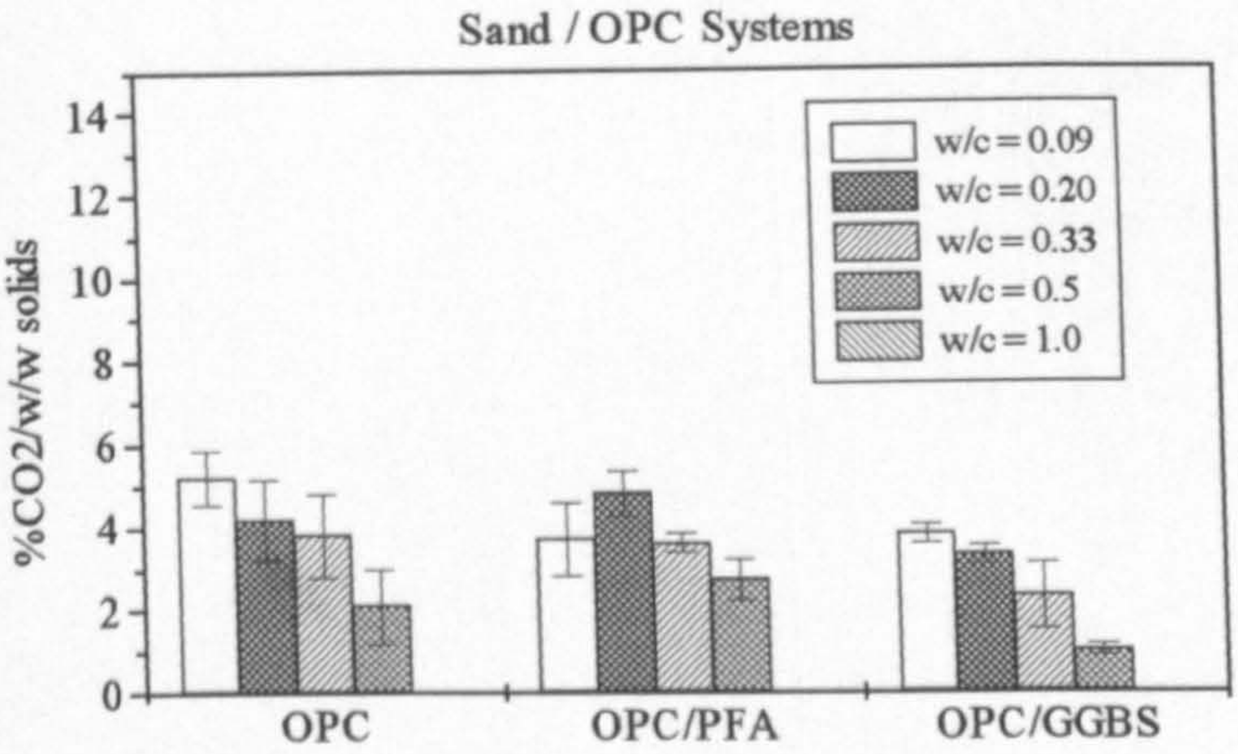
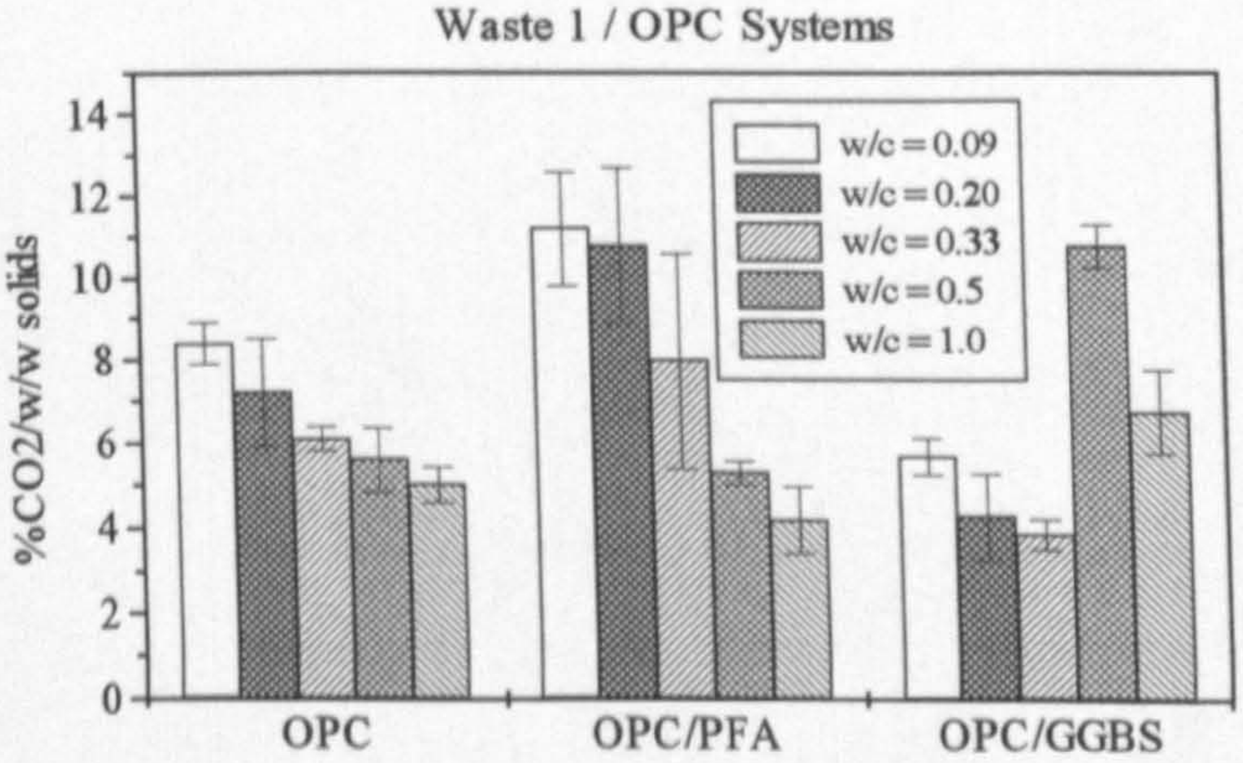


Figure 5.4g: Ternary diagrams for the different waste/binder systems showing the effect of mix proportions on the degree of carbonation

To further illustrate these results, Figure 5.5 shows the maximum CO_2 uptake in % by weight of solids after 100 minutes for selected mixes (16, 17, 18, 19 and 20).

The waste-free control specimens exhibited a relatively uniform behaviour for all types of binders examined. The total CO_2 uptake values for the overall samples were found between 0.1 and 6% of CO_2/w/w solids. Samples with the lower w/c ratios and higher cement content presented values more concentrated between 3 and 6% of CO_2/w/w solids. OPC showed to be slightly more reactive to carbon dioxide than SRPC and WOPC, presenting higher rates of carbonation in the overall results (values between 0.8 and 1.8 % CO_2/min.) and higher total uptake of carbon dioxide (values between 4 - 6% of CO_2/w/w solids). The following sequence is established: OPC>SRPC>WOPC. When the admixtures were added, in general, a slightly lower absorption of carbon dioxide was observed, though is possible to observe in samples 16 to 20 that when w/c ratio was





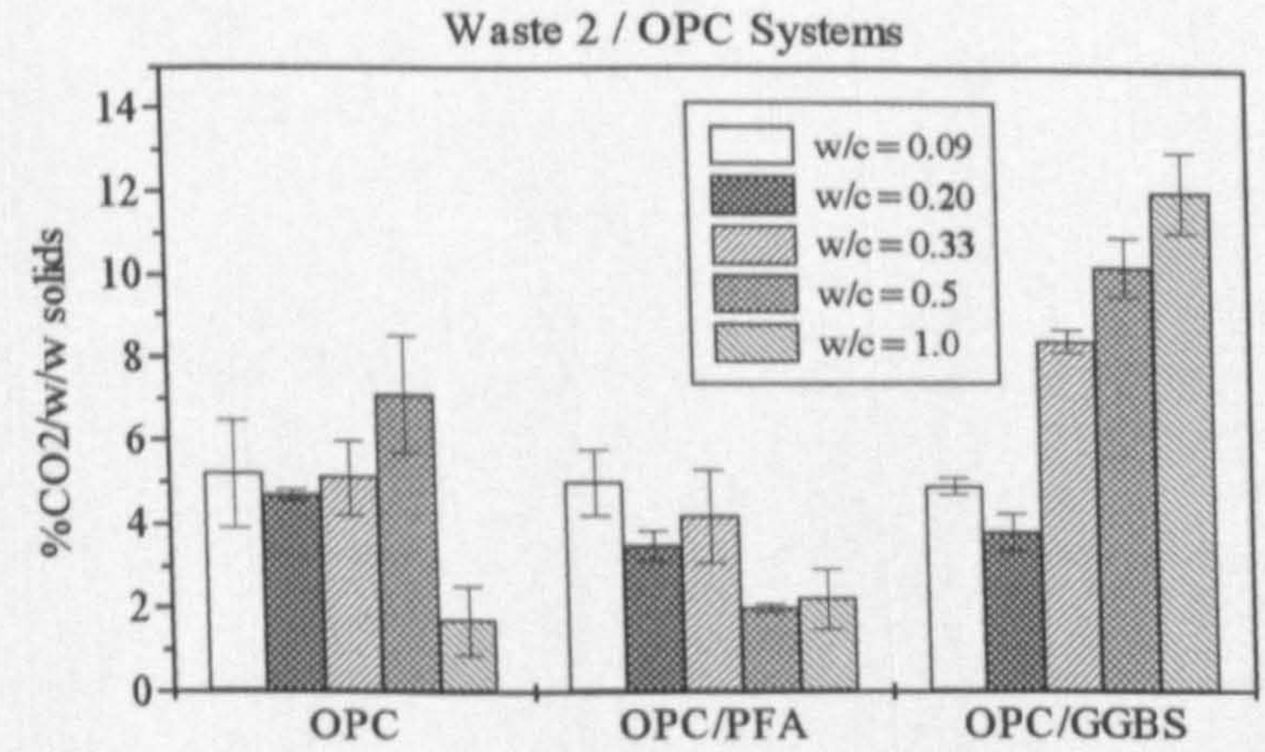
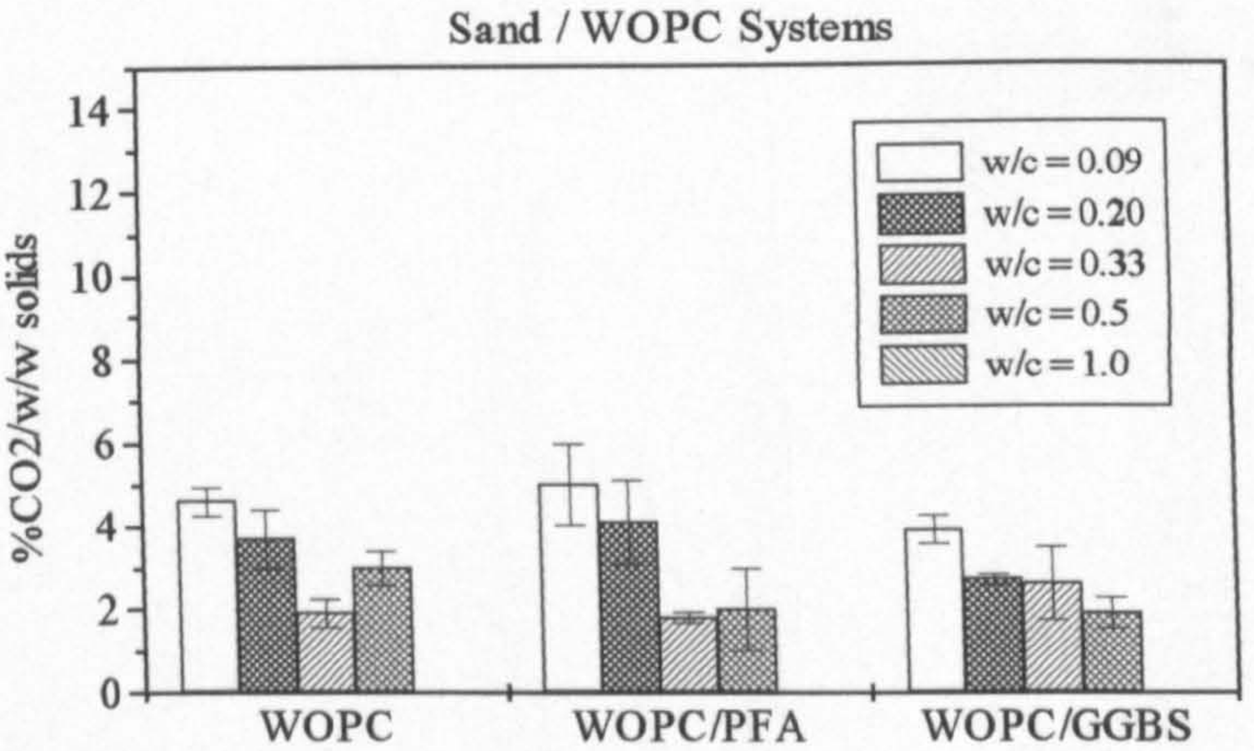
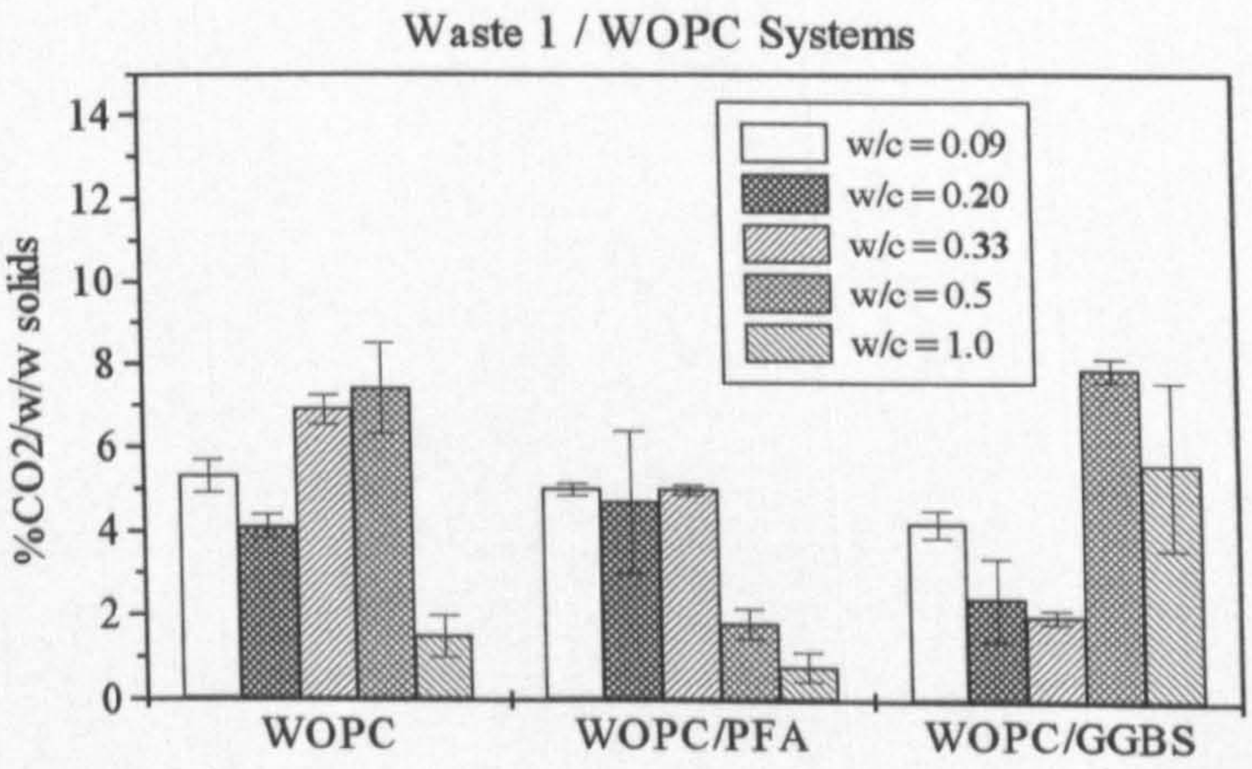


Figure 5.5a: Total carbon dioxide uptake after 100 minutes for selected mixes of different w/c ratios - OPC systems





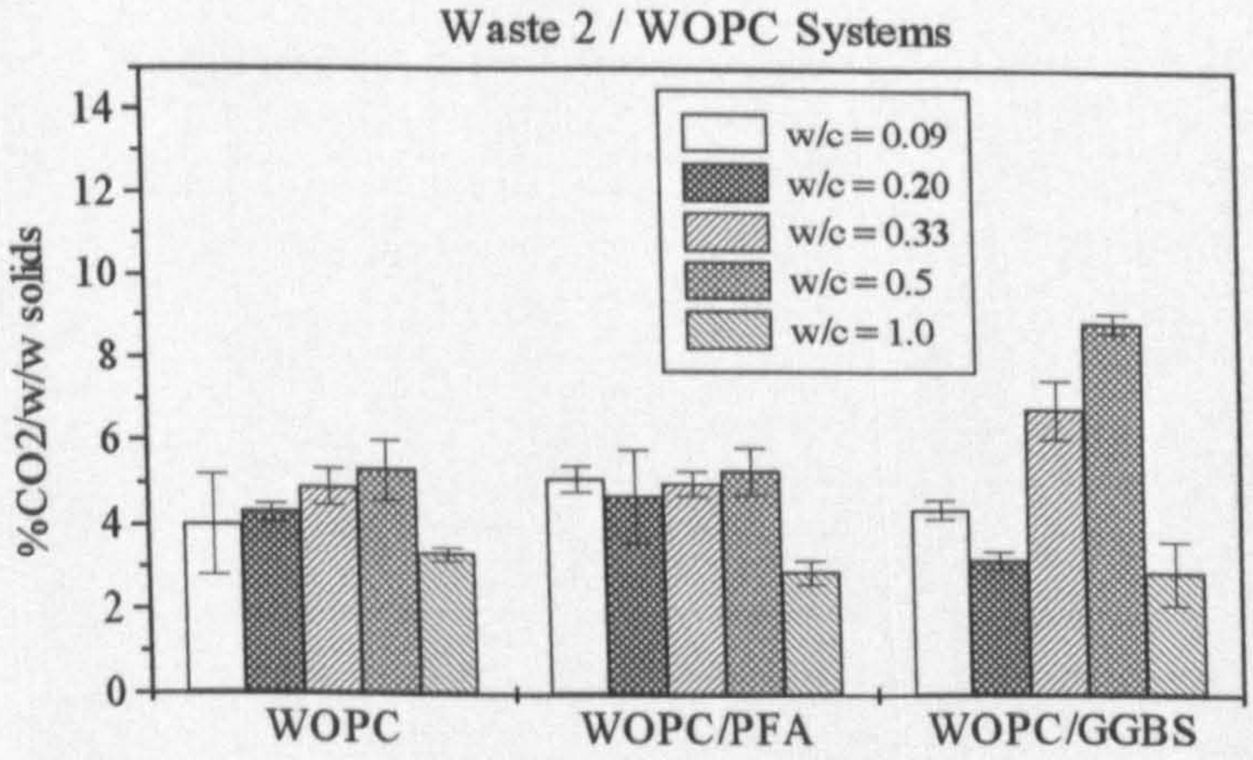
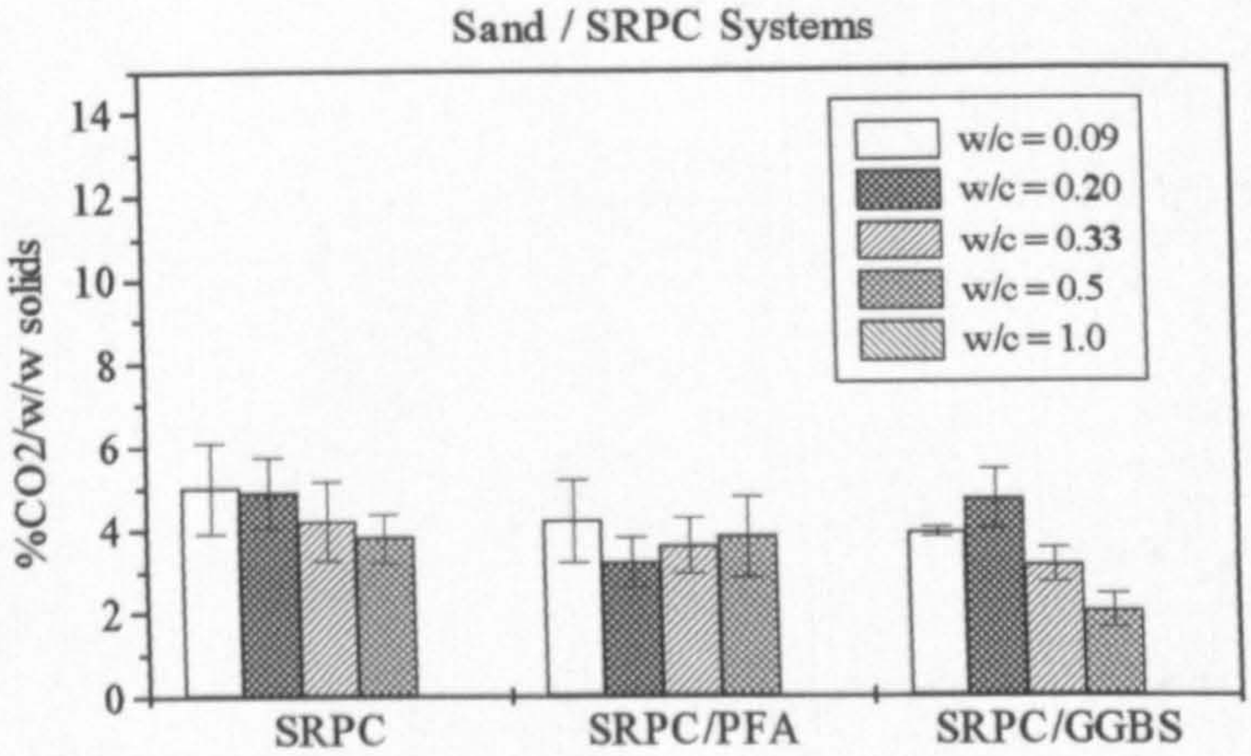
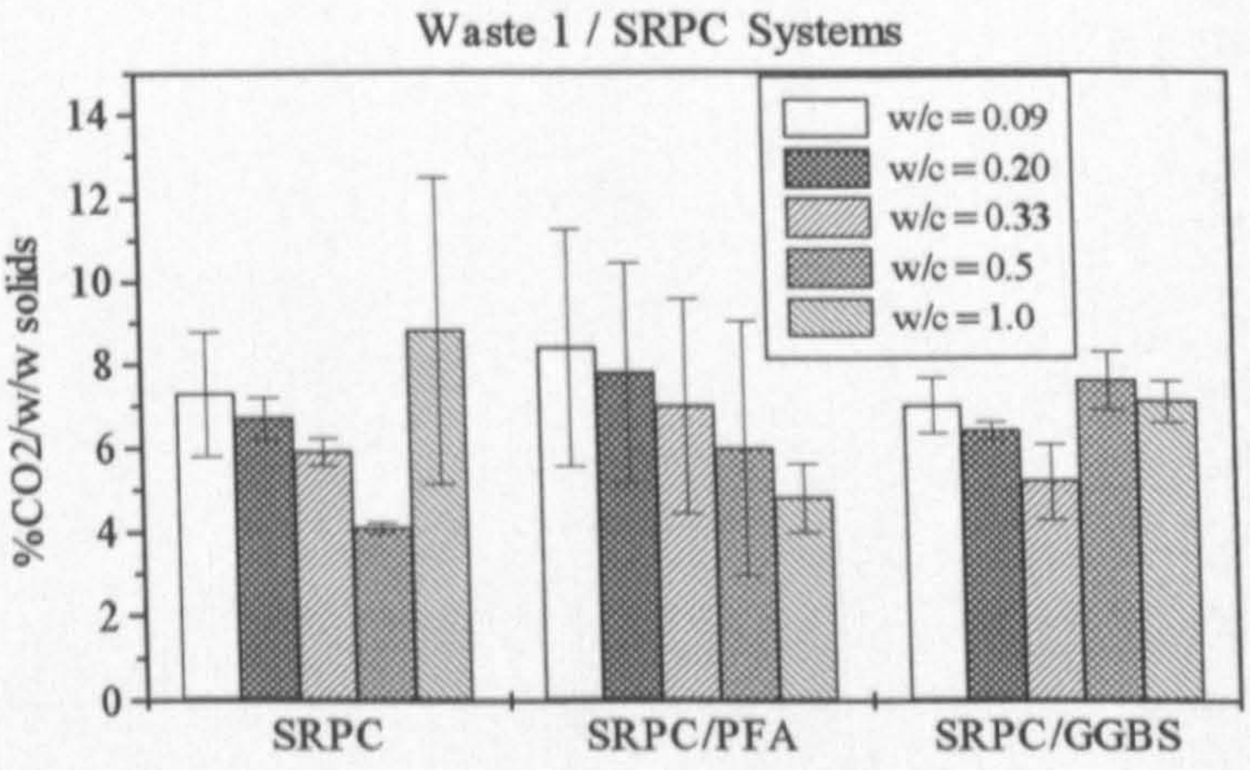


Figure 5.5b: Total carbon dioxide uptake after 100 minutes for selected mixes of different w/c ratios - WOPC systems





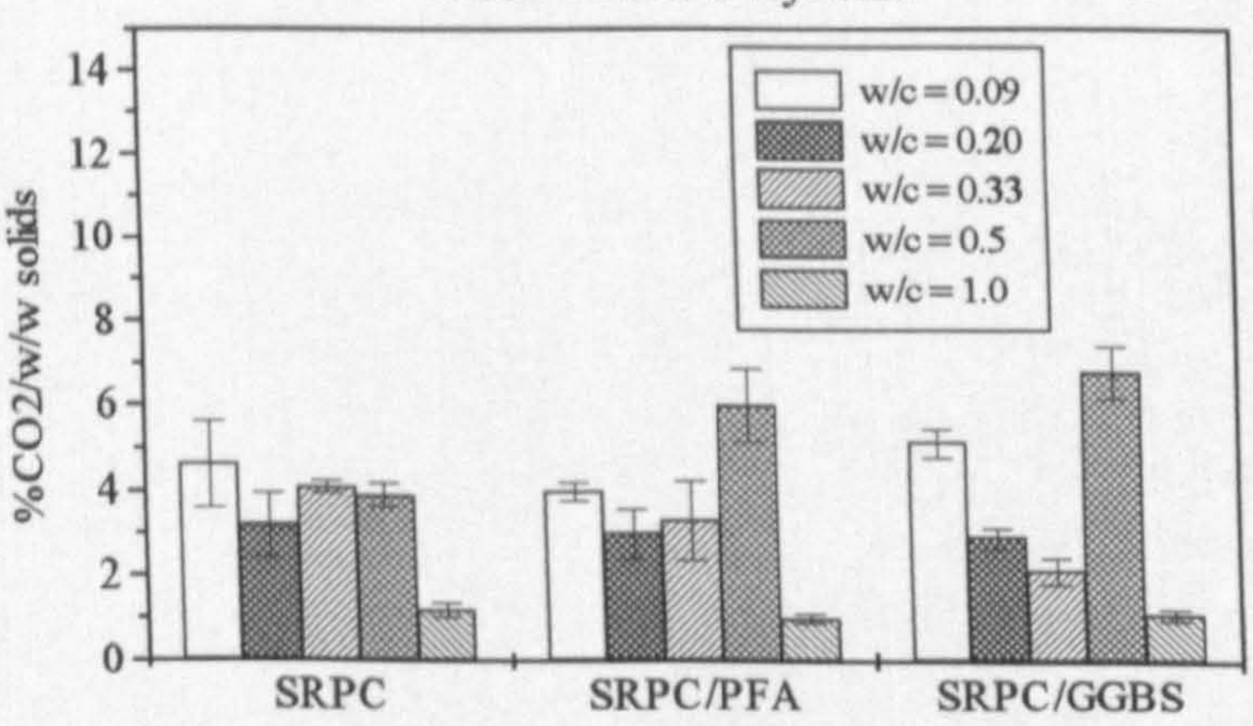


Figure 5.5c: Total carbon dioxide uptake after 100 minutes for selected mixes of different w/c ratios - SRPC systems

between 0.33 and 0.5 an improvement in the absorption of carbon dioxide occurred when compared to cement only.

When waste 1 was added to OPC (blended and non-blended) a marked change in the uptake of CO_2 occurred. For OPC and OPC/GGBS, the addition of the metal waste by up to 60% considerably increased the total amount of CO_2 consumed. For example, the highest value of 14.7 ± 1.8 % CO_2 / w/w solids (rate of carbonation = A = 0.41%/min.), was found for mix 13, OPC/W1, and 13.3 ± 0.52 % CO_2 / w/w solids (A = 0.30%/min.) for mix 19, OPC/GGBS/W1, at w/c ratios 0.66 and 0.50 respectively. OPC/PFA mixes were similar to the control as the maximum value of 11.2 ± 1.4 % CO_2 / w/w solids (A = 0.08%/min.) (mix 16), and w/c ratio at 0.09 was recorded. For OPC/W2 systems, the main differences were registered when slag was added. The higher values for carbon dioxide uptake of 10.2 ± 0.33% (A = 0.10%/min.) and 12.0 ± 0.78 % CO_2 / w/w solids (A = 0.08%/min.) were found at relatively higher w/c ratios of 0.5 and 1.0 for mixes 19 and 20, respectively.

WOPC/W1 samples showed a consistent carbon dioxide consumption for all specimens (blended and non-blended), with values for carbon dioxide uptake around 7.0 % CO_2 / w/w solids for the specimens that were highly carbonated. The highest values were registered for WOPC/GGBS/W1 at w/c ratios 0.5. When W2 was added no significant change was noted.

The results from SRPC/W1 mixes were very similar to those of OPC/W1, however, a general decrease of up to 3 to 4% of the maximum total uptake of CO_2 was registered. For W2, the addition of the pozzolans increased the uptake of the gas in comparison to SRPC by up to 6% at higher w/c ratios (0.5 and 1.0).

For almost all waste containing mixes the carbon dioxide uptake was 3 to 6% higher than for the control mixes. When PFA was used, the rate of carbonation was decreased significantly.

It was observed that the maximum rate of carbonation experienced was not necessarily proportional to the maximum CO_2 consumed (Fig. 5.3).

5.5 DISCUSSION

The influence of binder choice on the rate and total carbonation of selected cement-solidified wastes has been investigated. Carbonation has been found to be strongly influenced by the chemistry of the particular industrial waste, the type of cement/admixture and the w/c ratio, which determines the effective permeability and hence diffusity of carbon dioxide within a waste/binder system.

a) Waste composition and cement type

The addition of metal waste to the various cement pastes demonstrated an increased susceptibility to carbonation in the following order: OPC > SRPC > WOPC. OPC and SRPC gave higher values for total uptake of CO_2 after 100 minutes when compared to WOPC, although this occurred mainly when higher amounts of metal waste (up to 60% for waste 1) were used.

This suggests that the presence of certain cement phases, for example ferrite, in the cement may be important (ferrite is absent in WOPC) to the formation of ettringite, which in the presence of CO_2 normally decomposes to form gypsum, calcium carbonate and alumina gel (Nishikawa et al., 1992). Secondly, the presence of metal waste can influence the gas-permeability of a cement product (Poon et al., 1986), consequently causing an acceleration of the reaction of C_3S and formation of $CaCO_3$. Thirdly, waste forms containing the two metal wastes behaved quite differently on exposure to CO_2. Waste 2, in general, consumed less CO_2 than waste 1 indicating the concentration of specific metals or other waste species or unspecified physical effects within a waste might be important in governing the rate of the carbonation reaction. The presence of organic and anionic species could also have a influence in this respect by reacting with the cement paste and influencing the CO_2 diffusity.

b) Addition of mineral admixtures

The addition of PFA and GGBS also influenced total CO_2 uptake. PFA had little effect, except when used with WOPC/W2 where a reduced rate of CO_2 consumption was observed. GGBS gave the highest CO_2 uptake above a w/c ratio of 0.5, for all cement/waste systems examined and might be due to some microstructural changes in the C-S-H phase (topochemical precipitation of gel) as some authors have shown that the microporosity inside this product is enhanced by presence of CO_2 (De Ceukelaire et al., 1993). GGBS/cement pastes contains less calcium hydroxide than Portland cement and consequently a reaction between C-S-H and CO_2 may become more pronounced. One could suggest that as more C-S-H becomes involved in the carbonation process there is a consequent precipitation of calcium carbonate accompanied by a sharper decrease in the pore volume as against other systems.

c) Moisture content

The amount of water in the waste/binder system is crucial for carbonation to proceed at an optimum rate. Water is necessary for a reaction with CO_2, but too much water severely limits the rate of the reaction. In other words, as pores are filled with water, the penetration of carbon dioxide is hindered as the rate of diffusion of CO_2 is reduced; if on the other hand pores are completely dry the reaction of CO_2 is absent. Therefore, this implies that solvation of carbon dioxide is critical for effective carbonation to proceed. It is also shown that different water contents are required for different cement types which, in return is related to the specific surface area of individual cements. Figure 5.3 illustrates these effects by showing the increased delay in induction time in the carbonation reaction as water content increases.

5.6 SUMMARY AND CONCLUSIONS

In this Chapter the effects of variations in the mix parameters, namely w/c ratio, cement type, waste concentration and type of mineral admixture on the rate and total amount of carbonation of waste forms have been examined.

The main conclusions are:

a) cement pastes blended with the industrial wastes react with carbon dioxide in higher proportions than cement paste only;
b) the reactivity of different cements varies in the presence of CO_2, following the sequential order: OPC>SRPC>WOPC;
c) the complexity of industrial wastes (presence of different anions, organics and a wide range of metals) has a strong influence on the rate and total amount of carbonation, and W1 showed higher values for total uptake of CO_2 than W2 specimens;
d) pastes containing waste and pozzolans were found to be vulnerable to carbonation and this phenomenon can aid the immobilisation of certain metals in waste form. In addition, GGBS affects the carbonation reaction, which increases with water content greater than w/c= 0.5;
e) carbon dioxide uptake generally decreases with an increase in w/c ratio.

The objective of the following Chapter is to explore the physico-chemical properties of samples that used mix designs found to be in the highly carbonated areas and compare against other specimens prepared with mix designs known to be in the moderate and poor carbonated areas. This study will be fundamental for the evaluation of the accelerated carbonation reaction process and its effects upon waste forms.

CHAPTER 6

THE EFFECT OF ACCELERATED CARBONATION ON THE PROPERTIES OF CEMENT SOLIDIFIED WASTE FORMS

6.1 PREVIEW

The previous Chapter has examined the kinetics of the carbonation reaction through the measurement of total carbon dioxide uptake and/or rate of carbonation of different waste/binder systems. The effects of influence of the industrial waste composition, cement type, addition of mineral admixtures and moisture content were discussed. Areas showing different degrees of carbonation were delineated, however, the properties of the specimens prepared under these different fields were not discussed.

The objective of this Chapter is to investigate the physico-chemical properties of specimens prepared using mix designs found to be in the highly, moderately and poorly carbonated areas and draw a comparison between these carbonated samples and their respective non-carbonated analogues.

Ordinary Portland cement (blended and non-blended) was the binder chosen for this study. Specimens were prepared and cured, either in an accelerated carbonation regime or in nitrogen, and analysed physically, chemically and microstructurally after 28 days. The results show that by controlling mix parameters during carbonation, it is possible to optimise the immobilisation of specific metals.

6.2 MATERIALS AND EXPERIMENTAL METHODS

The materials used (OPC, PFA, GGBS, Cory waste - W1 and Metal Colours waste - W2) are described in Chapter 2. The dried wastes were mixed with cement, mineral admixtures and double-distilled water using a mechanical mixer at a fixing mixing time. Mix designs are given in Table 6.1. The samples chosen were the highly carbonated area

(A), and poorly carbonated area (B and C) from the mix designs previously examined in Figure 5.4a-g (Chapter 5).

Table 6.1: Mix designs for the selected samples

Samples	OPC%	PFA%	GGBS%	Water%	W1%	w/b**	w/s**
1W1A***	30	-	-	30	40	1.0	0.43
1W1B	40	-	-	10	50	0.25	0.11
1W1C	35	-	-	35	30	1.0	0.54
2W1A	42.5	7.5	-	15	35	0.3	0.2
2W1B	29.75	5.25	-	15	50	0.43	0.18
2W1C	34	6	-	25	35	0.62	0.33
3W1A	18	-	12	20	50	0.66	0.25
3W1B	30	-	20	20	30	0.4	0.25
3W1C	12	-	8	35	45	1.75	0.54
Samples	OPC%	PFA%	GGBS%	Water%	W2 %	w/b**	w/s**
1W2A***	50	-	-	15	35	0.3	0.18
1W2B	45	-	-	25	30	0.55	0.33
1W2C	25	-	-	30	45	1.2	0.43
2W2A	42.5	7.5	-	15	35	0.3	0.18
2W2B	38.25	6.75	-	25	30	0.55	0.33
2W2C	21.25	3.75	-	30	45	1.2	0.43
3W2A	24	-	16	25	35	0.62	0.33
3W2B	30	-	20	30	20	0.6	0.43
3W2C	18	-	12	20	50	0.6	0.25

Note: ** w/b = water/binder ratio; w/s = water/solids ratio
*** A = mix design chosen from the optimum carbonated zones; B and C = mix designs chosen from outside the optimum areas (Figure 5.4a-g).

Six samples were cast from each mix in 32mm x 32mm cylindrical PVC moulds. Half of them were cured in nitrogen and the other half were placed in a chamber filled with CO_2 which was refilled periodically to avoid CO_2 starvation. After 1 hour the CO_2 samples were removed to the ambient (laboratory) environment. The room temperature and humidity were constantly monitored, and they were: 21°C ± 3 and Rh 57% ± 6. Control (waste-free) specimens (50% OPC, 30% sand and 20% water) were also prepared and cured under both regimes. Samples left in nitrogen-environment were demoulded after 1 day, while samples cured under the accelerated carbonation program could be demoulded after 10 to 20 minutes. After 28 ± 3 days the samples were tested for strength, microcharacterisation and leachate composition using methods described in Chapter 2.

6.3 RESULTS

6.3.1 Strength Characteristics

The results for all the curing exposure conditions for the different waste/binder types are shown in Table 6.2. Generally, an increase in compressive strength for the specimens was observed when the material was exposed to gaseous CO_2.

The cement paste only (control) sample gave the highest recorded strength, as might be expected, with the value for CO_2 cured sample being 55% higher than the nitrogen cured one. When the waste was added these values decreased dramatically. However, strengths were 45% greater for W1 and W2 when they were carbonated. Sample 1W1A (40% waste 1), which was carbonated under optimised conditions gave the highest value of 7.9 MPa.

The increase in strengths observed after carbonation varied depending on the mix parameters selected. Significant differences were found for waste forms carbonated under optimised conditions. For W1A samples, an increase in strength by 30 to 35% and 70 to 75%, from B and C (non-optimised) respectively, was observed for all binders. Samples blended with OPC/PFA gave the lowest values. For W2, the strengths were lower than W1. Nevertheless, a significant strength increase for carbonated samples was recorded, except when PFA was used (2W2A). It was noted that the GGBS promotes a reaction with carbon dioxide, resulting in considerable strength values, for example 7.2 MPa (3W1A) and 4.1 MPa (3W2A).

Table 6.2: Strength results for all mixes

Sample	Environment	UCS (MPa) mean of three values	ESD*	CV**(%)
1W1A	N_2	1.0	±0.25	25.0
	CO_2	7.9	±1.25	15.8
1W1B	N_2	2.7	±0.12	4.63
	CO_2	5.1	±0.10	1.96
1W1C	N_2	2.0	±0.07	3.75
	CO_2	2.8	±0.10	3.57
2W1A	N_2	2.9	±0.10	3.45
	CO_2	3.3	±0.07	2.12
2W1B	N_2	1.5	±0.17	11.3
	CO_2	2.5	±0.05	2.0
2W1C	N_2	1.3	±0.12	9.23
	CO_2	0.7	±0.17	24.3
3W1A	N_2	3.7	±0.10	2.70
	CO_2	7.2	±0.17	2.36
3W1B	N_2	2.1	±0.10	4.76
	CO_2	4.9	±0.17	3.47
3W1C	N_2	1.0	±0.12	12.0
	CO_2	1.4	±0.12	8.57
1W2A	N_2	0.5	±0.05	10.0
	CO_2	1.7	±0.07	4.12
1W2B	N_2	0.9	±0.15	16.7
	CO_2	2.0	±0.10	5.0
1W2C	N_2	0.6	±0.10	16.7
	CO_2	0.8	±0.20	25.0
2W2A	N_2	0.4	±0.07	17.5
	CO_2	2.2	±0.15	6.82
2W2B	N_2	1.3	±0.10	7.69
	CO_2	2.0	±0.12	6.0
2W2C	N_2	0.7	±0.12	17.14
	CO_2	1.1	±0.07	6.36
3W2A	N_2	1.6	±0.07	4.37
	CO_2	4.1	±0.12	2.93
3W2B	N_2	1.0	±0.10	10.0
	CO_2	2.1	±0.07	3.33
3W2C	N_2	0.8	±0.12	15.0
	CO_2	1.0	±0.12	12.0
Control	N_2	15.2	±0.57	3.78
	CO_2	34.3	±4.25	12.4

Note: * Estimated Standard Deviation; ** Coefficient of Variance

6.3.2 Microcharacterisation Tests

Phase Distribution

Table 6.3 shows the main crystalline phases associated with carbonation as identified by X-RD at 28 days of age. The results, based on a comparison of the intensity of the principal diffraction lines for each set of sample, show that the amount of calcite increased when carbon dioxide curing was carried out. Ettringite appeared to decompose on exposure to carbon dioxide with a consequence increase in proportion of calcite and gypsum. The amount of C_3S appeared to decrease in the presence of carbon dioxide,

indicating an acceleration of the hydration of C_3S as already reported (Lange et al., 1996a).

Table 6.3: Qualitative X-ray results

Sample	Environment	Calcite	Gypsum	Ettringite	C_3S
1W1A	N_2	72	16	67	88
	CO_2	301	49	na	78
1W1B	N_2	190	31	62	46
	CO_2	203	66	27	52
1W1C	N_2	140	na	36	137
	CO_2	174	na	na	83
2W1A	N_2	166	26	74	79
	CO_2	194	27	54	41
2W1B	N_2	116	11	34	105
	CO_2	184	17	na	52
2W1C	N_2	111	56	62	72
	CO_2	113	58	49	56
3W1A	N_2	93	na	75	61
	CO_2	277	89	na	41
3W1B	N_2	86	na	32	98
	CO_2	184	19	na	60
3W1C	N_2	79	18	21	122
	CO_2	117	14	na	103
1W2A	N_2	144	na	42	150
	CO_2	210	22	na	95
1W2B	N_2	117	20	41	58
	CO_2	215	24	36	66
1W2C	N_2	100	65	85	60
	CO_2	123	69	71	22
2W2A	N_2	81	21	39	96
	CO_2	157	17	39	na
2W2B	N_2	92	19	66	106
	CO_2	140	15	na	98
2W2C	N_2	80	20	35	79
	CO_2	117	14	30	na
3W2A	N_2	96	88	82	80
	CO_2	277	151	22	77
3W2B	N_2	90	20	29	86
	CO_2	175	19	25	na
3W2C	N_2	81	26	12	227
	CO_2	96	28	na	120
Control	N_2	51	42	135	229
	CO_2	478	59	na	62

Note: calcite (1.88Å); C_3S (2.19Å); gypsum (7.56Å); ettringite (9.7Å) in cps. na = result not available

The main carbonate phase generally found was calcite, however, vaterite was also detected in some samples containing GGBS (3W1B, 3W1C, 3W2B).

SEM Observations

The morphology of both solidified industrial wastes with blended and non-blended OPC/binders were very similar when carbonated. Plates 6.1 to 6.8 show backscattered electron image (BEI) micrographs of non-carbonated and carbonated control, industrial waste/OPC mixes.

For carbonated samples, the microstructure was typified by the development of abundant calcite in pores. The morphology of C-S-H differs from samples hydrated under a nitrogen environment as typified by, for example plates 6.1 and 6.3. The irregular calcite crystallites shown on Plates 6.3, 6.4 and 6.8 appear to co-exist with C-S-H structure.

In the OPC/waste samples, C-S-H seems to have poorly formed laths, being difficult sometimes to distinguish morphologically from calcite (Plate 6.6). Apparently, the reaction products of these samples when carbonated consist of a more fairly dense material than when left in nitrogen, in which a calcium rich material can be distinguished covering unreacted cores (Plate 6.7). It must be noted the high porosity of the samples (Plate 6.6 and 6.7), probably due to the intense precipitation of calcite products.

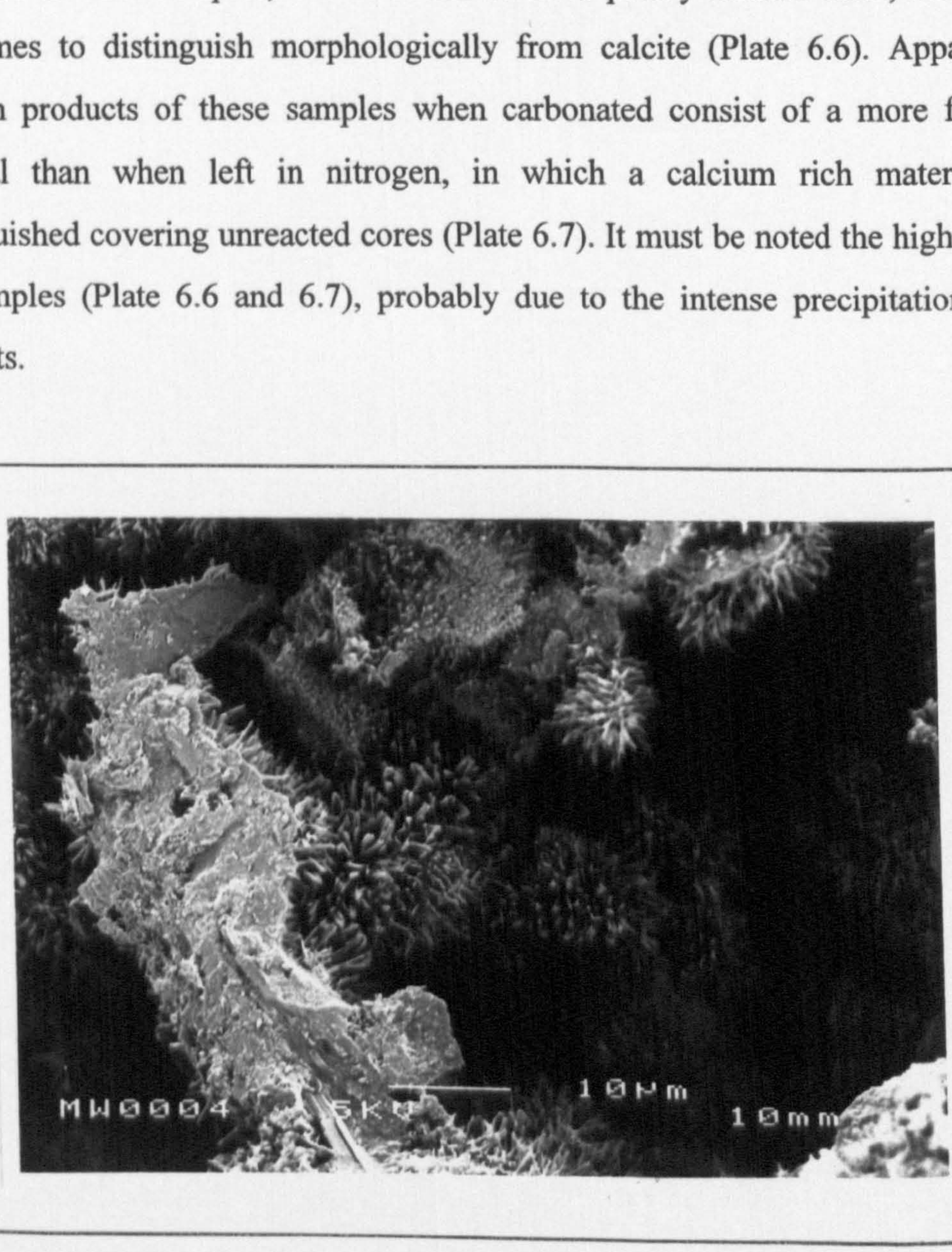


Plate 6.1: Fracture sample of a non-carbonated OPC (Control) specimen - typical C-S-H structure showing some ettringite

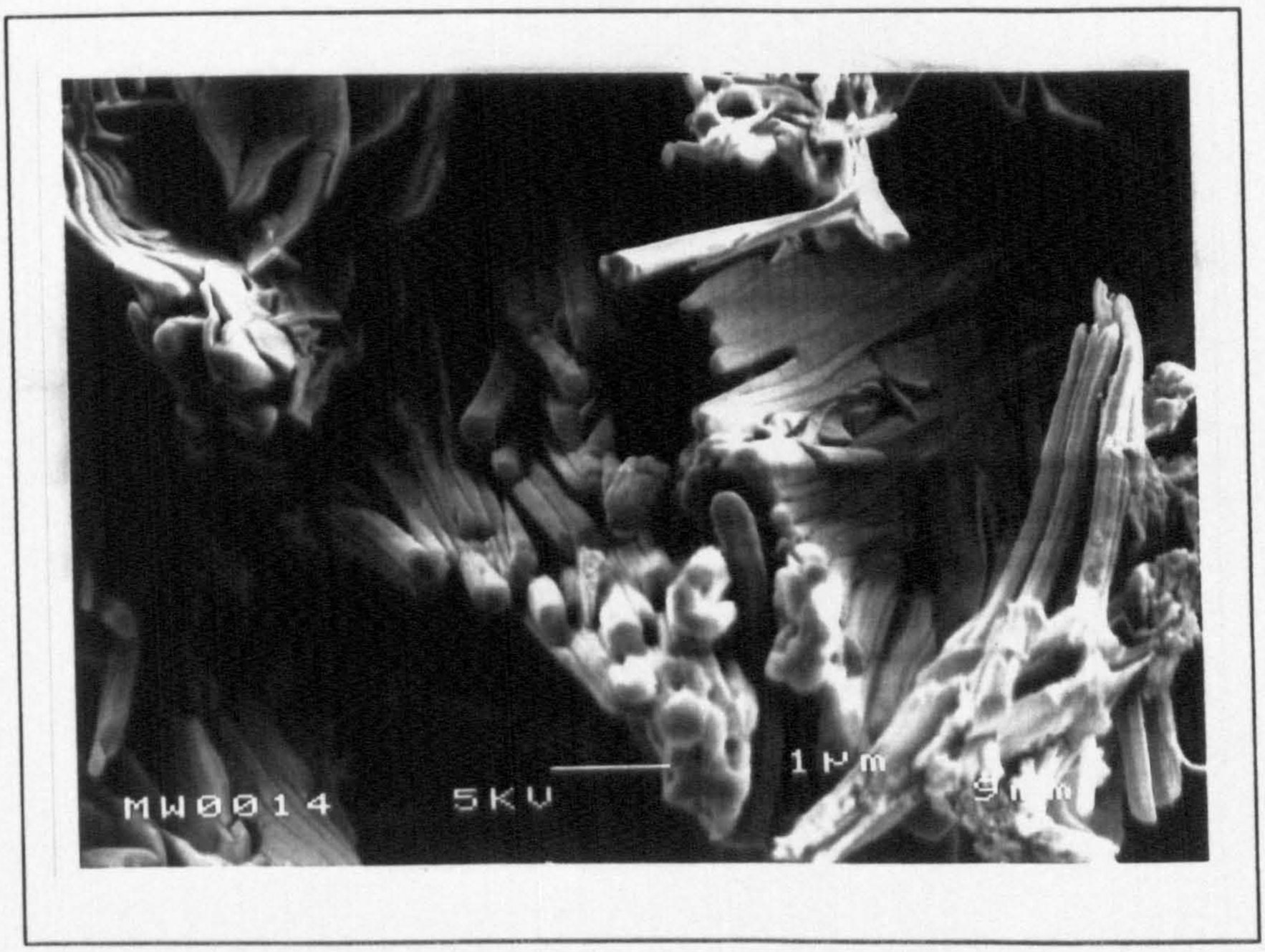


Plate 6.2: Same as 6.1 showing details of the ettringite structure

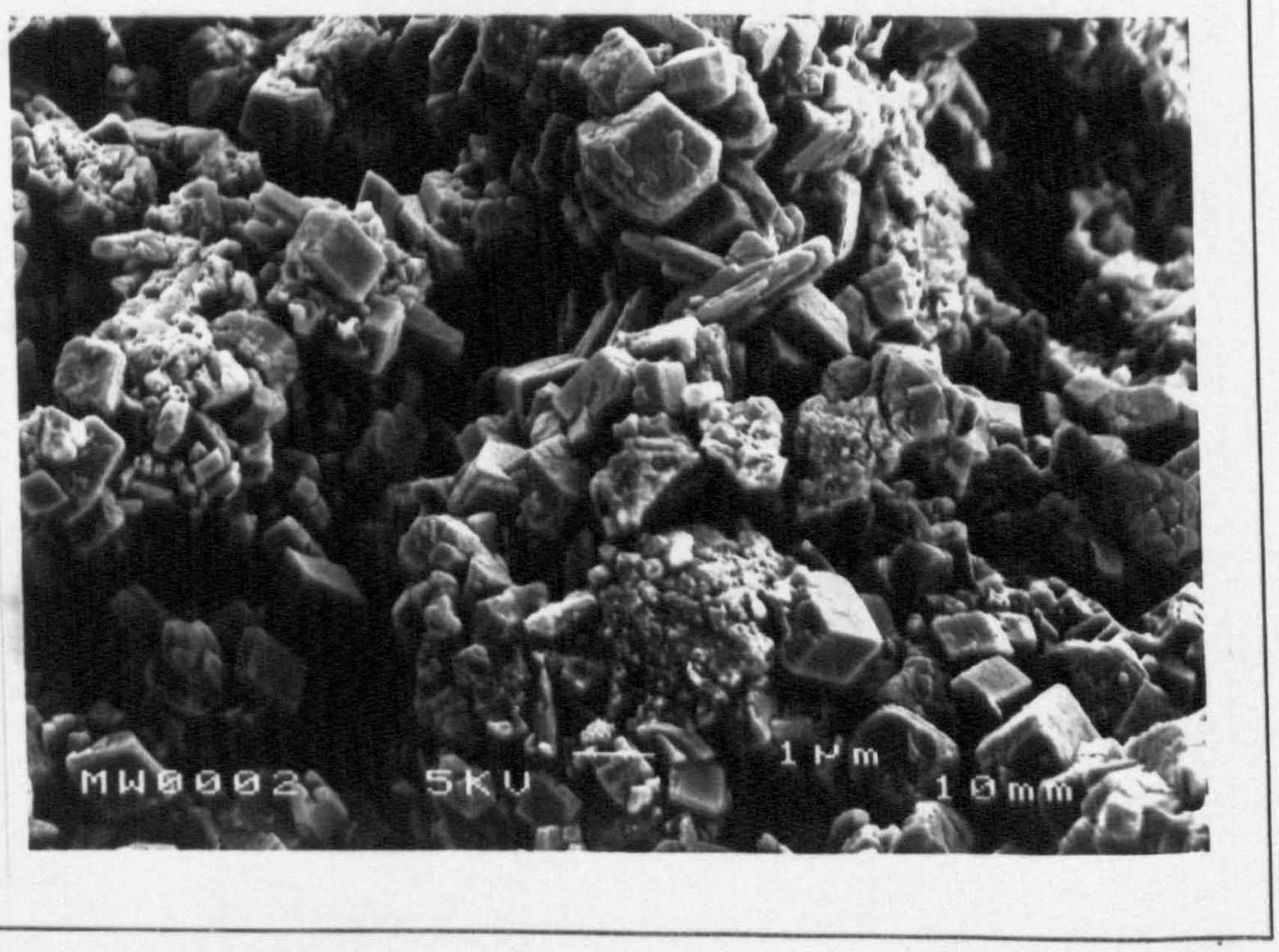


Plate 6.3: Fracture sample of a carbonated OPC (control) showing close up of calcite crystallites (rhombs)

Plate 6.4: Same as 6.3 showing pseudomorph calcite structure

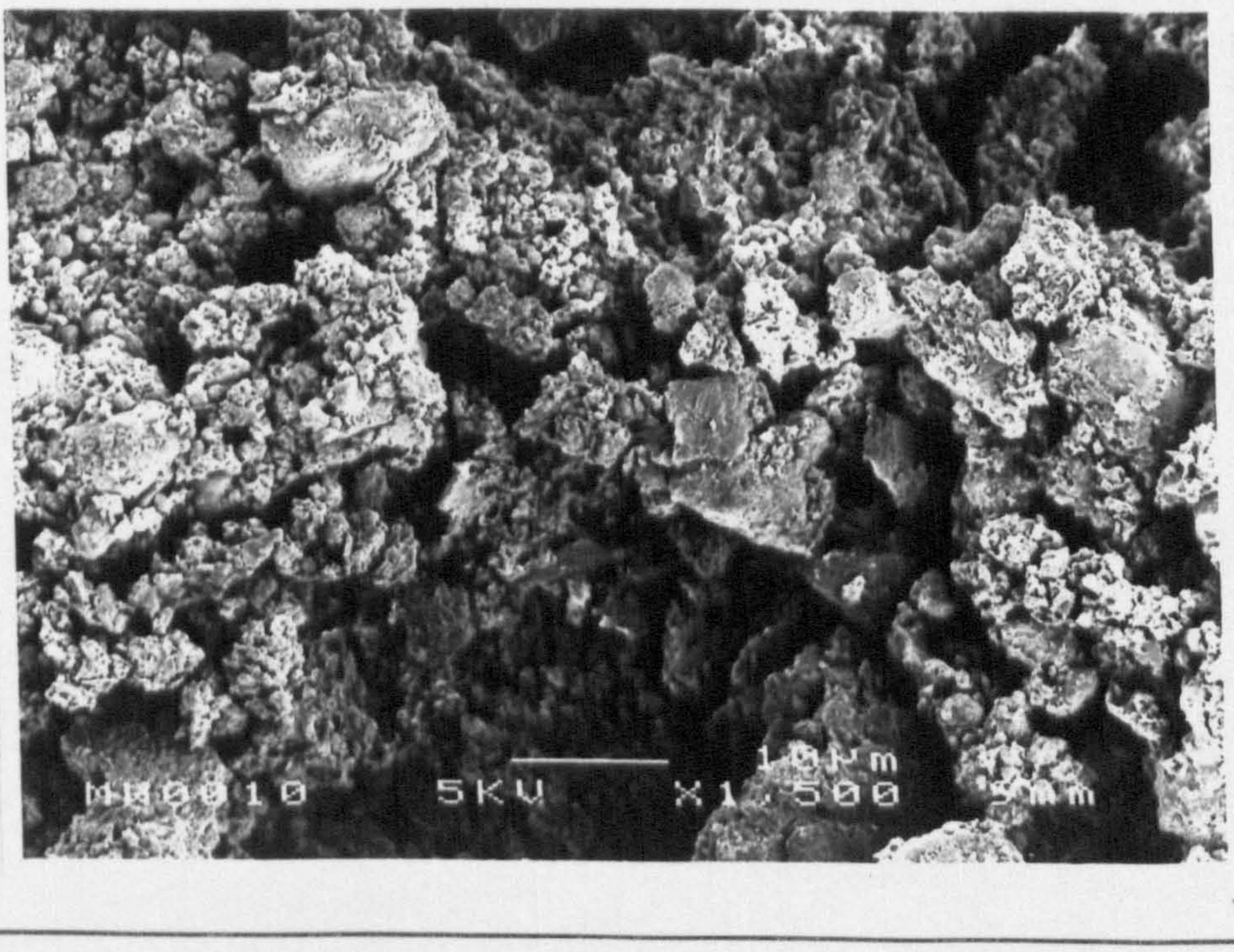


Plate 6.5: Fracture sample of a non-carbonated OPC/industrial waste specimen - showing the poor development of hydration products

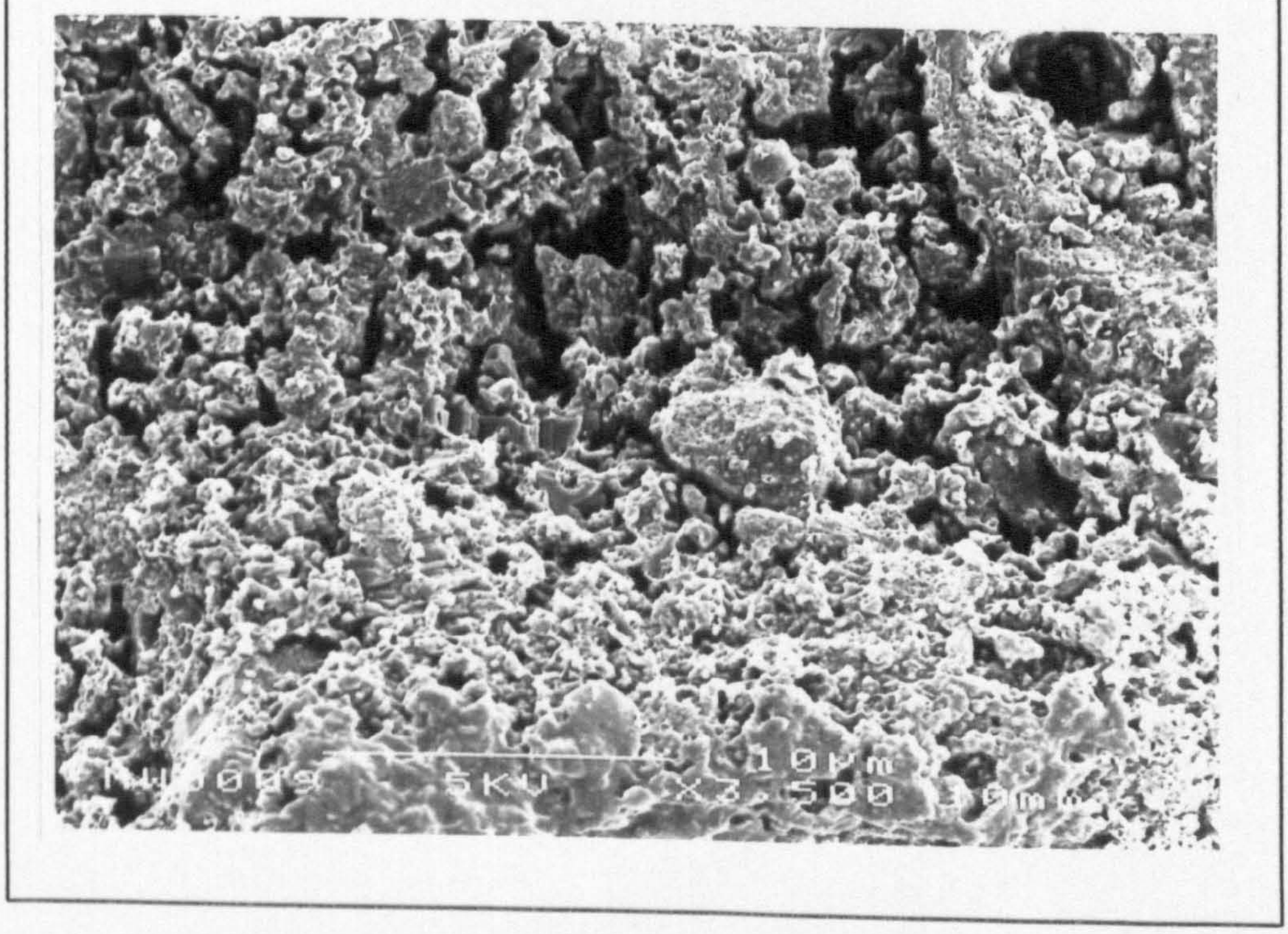


Plate 6.6: Fracture surface showing typical example of carbonated OPC/industrial waste specimen

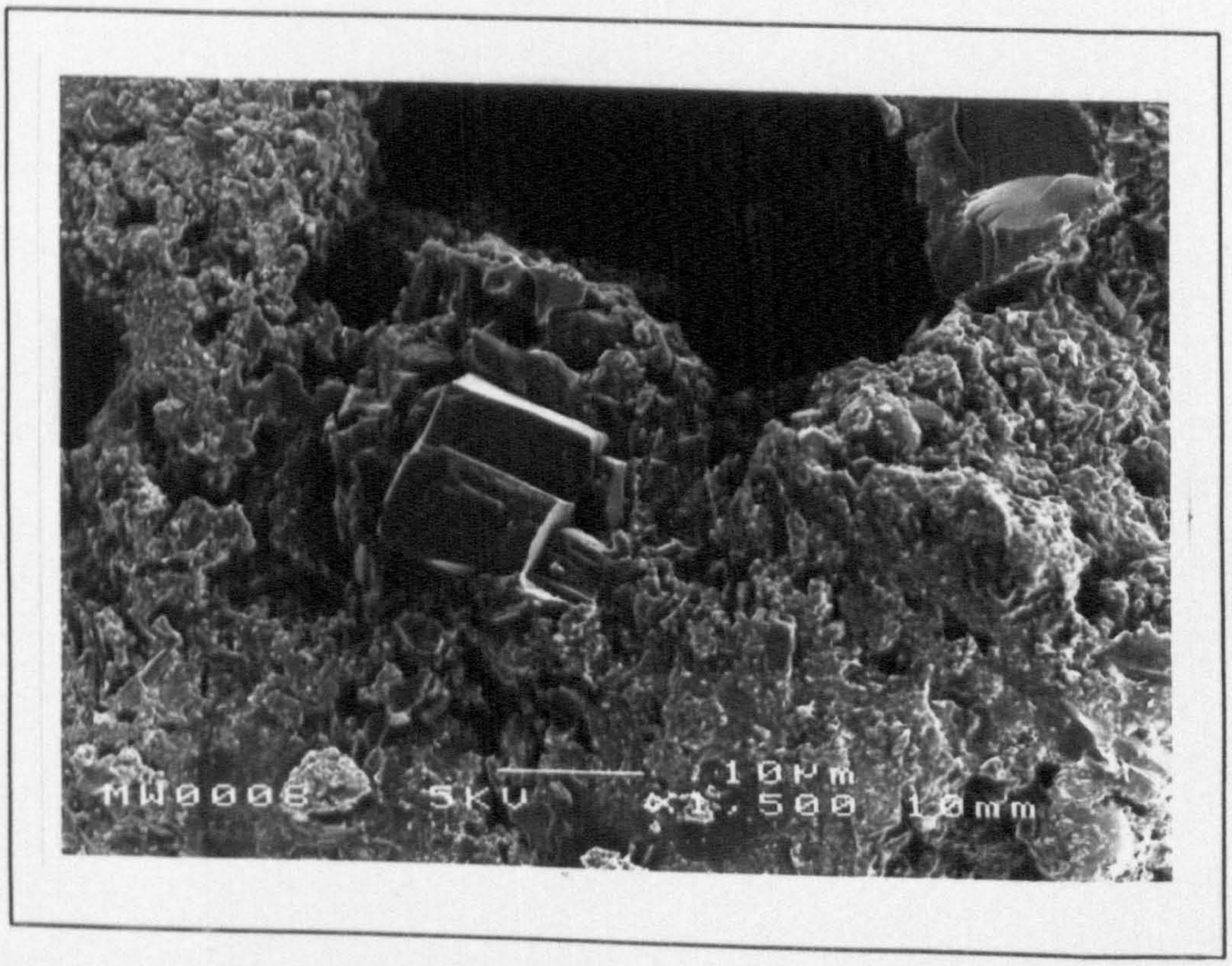


Plate 6.7: Fracture sample of a carbonated OPC/industrial waste specimen showing a pore structure blocked with calcium rich material

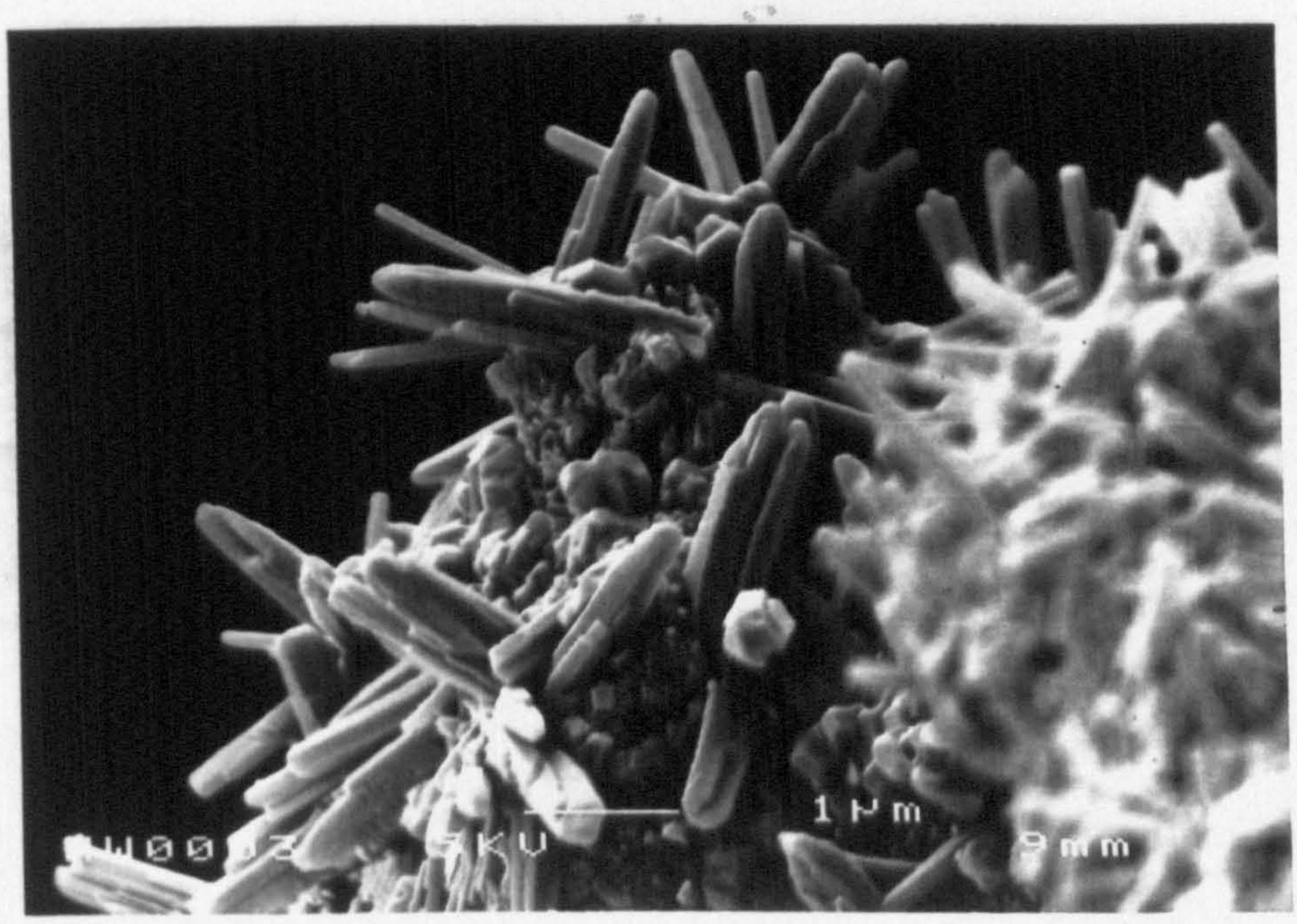


Plate 6.8: Fracture sample of a carbonated OPC/industrial waste specimen showing calcite crystallite within a pore

The irregular calcite crystallites seen above can be compared, as an illustration, to Figure 6.1 which gives the true structure of calcite. The relationship between the morphological (cleavage rhomb) pseudo-cell and the true unit cell of calcite is well shown.

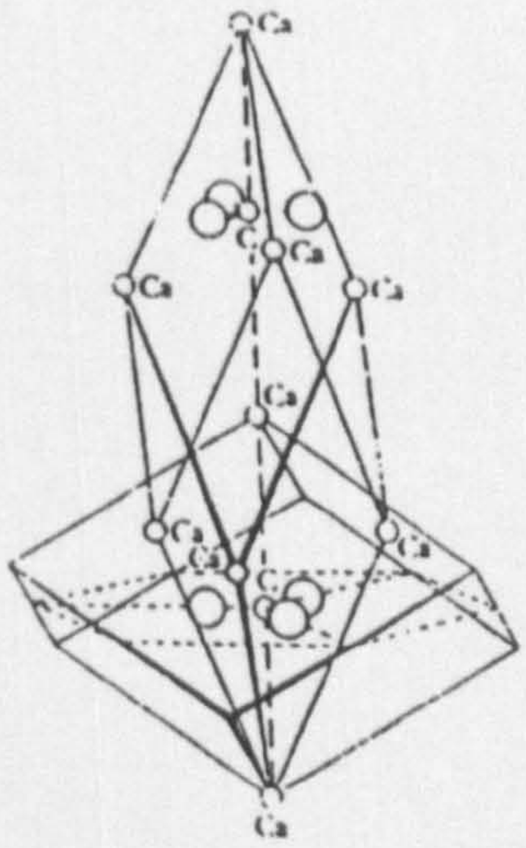


Figure 6.1: The structure of calcite (after Deer et al., 1978)

Plates 6.9 to 6.12 show BSE images of polished samples of mixes 1W1A and 2W1A. Typically residual clinker grains were enveloped by a silica rich rim surrounded by calcium carbonate which also infills porosity. EDAX analysis revealed the higher apparent concentration of metals such as Pb and Zn inside the Si-rich rims together with higher than usual amounts of potassium (1.5 - 4.0%). Other metals such as Ni, Zn and Cr appeared to be preferentially located in either the filled porosity or decalcified C-S-H/calcium carbonate matrix. Appendix D gives the microprobe analyse associated with this work.

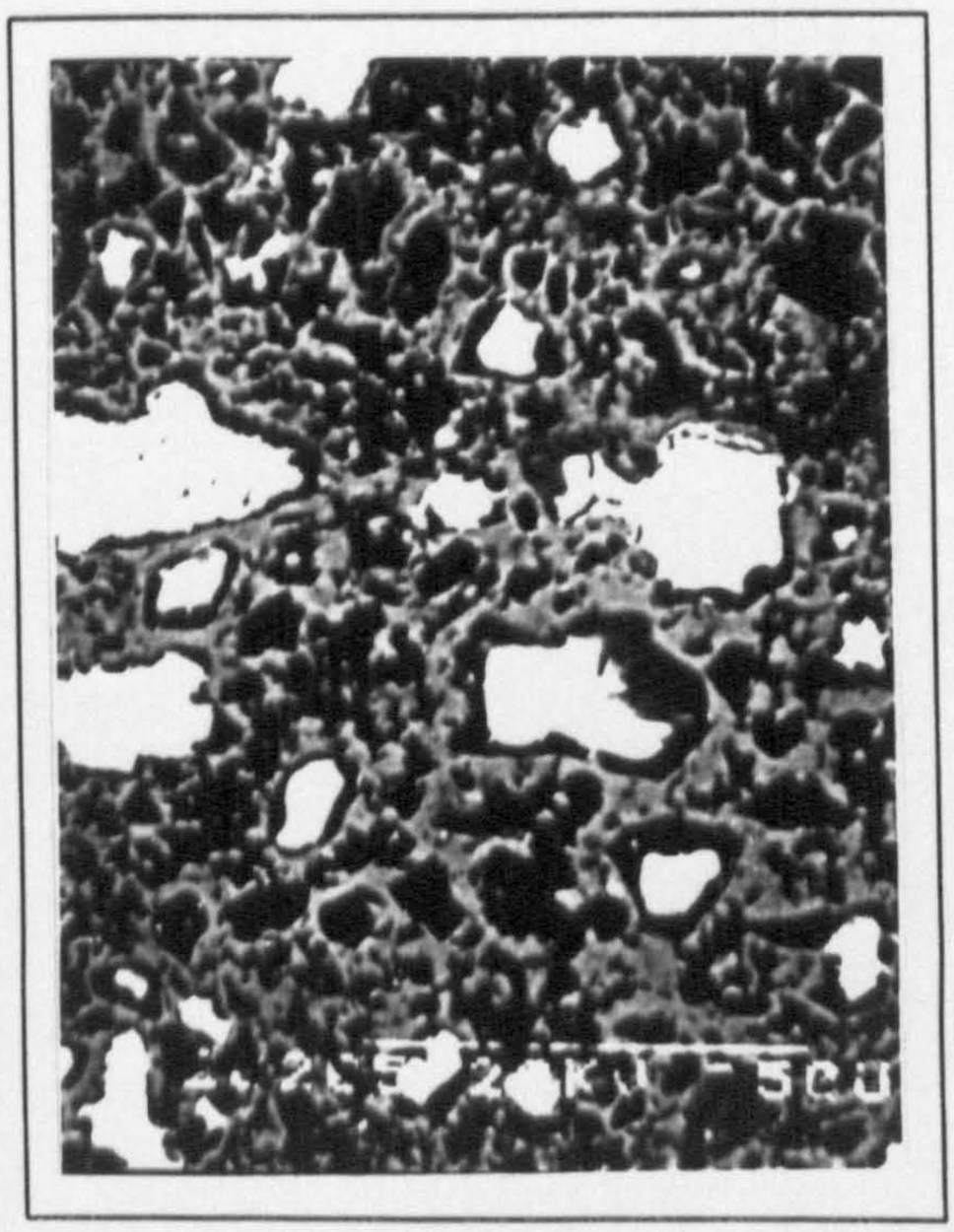


Plate 6.9

Plate 6.10

Explanation of the Plates:

Plate 6.9: Polished sample - 1W1A/carbonated and showing light coloured cement clinker grains, surrounded by a Si-rich dark rims. Calcite is grey and porosity is black.

Plate 6.10: Same sample as above, showing details of rim development

Plate 6.11

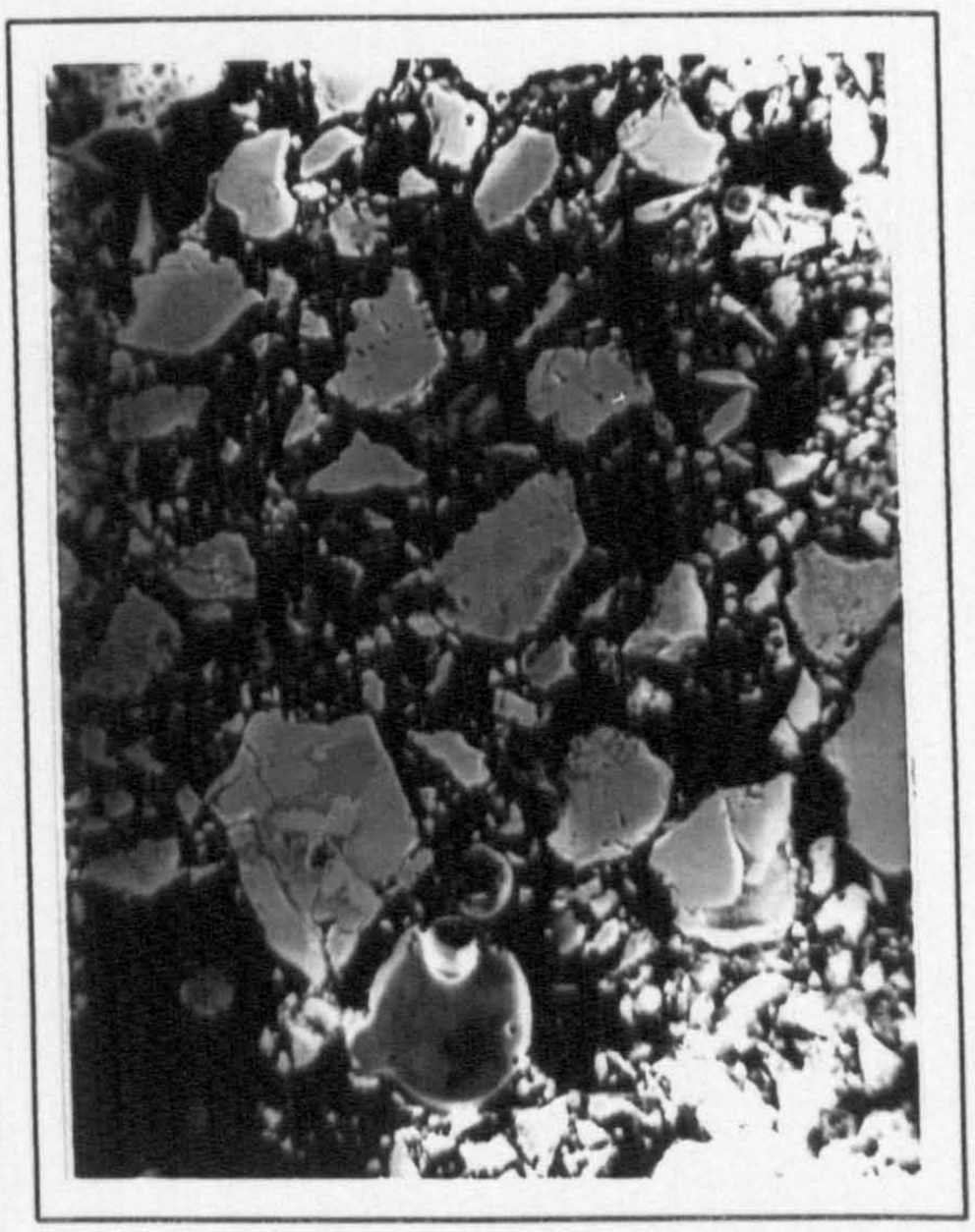


Plate 6.12

Explanation of the Plates:

Plate 6.11: Polished sample - 2W1A/carbonated showing the same features as 6.9 as well as PFA particles

Plate 6.12: Polished sample - 2W1A/non-carbonated showing a poorly developed hydration

FTIR Analysis

FTIR results are summarised for OPC/waste specimens only in Table 6.4. Details of spectrums are given in Figure 6.2.

The principal products found during OPC hydration are C-S-H, calcium hydroxide and ettringite/monosulphate. A close examination of the results suggests that differences can be attributed to the effect of waste addition as well as to the effect of carbonation on the hydration of the cement.

Table 6.4: Infrared spectral data for industrial wastes systems, where NC = non-carbonated and CA = carbonated

Sample	SiO_4^{4-} (v3)	SiO_4^{4-} (v4)	H_2O v1+v2	OH $Ca(OH)_2$	HOH (v2)	SO_4^{2-} (v3)	CN^-	Al-O	SiOH	CO_3^{2-} (v3)	CO_3^{2-} (v2)
C-NC	963	525	3423	3645	1655	1116	-	-	-	1420	874
C - CA	980	514	3407	-	1684	1028	-	-	-	1438	874
1W1A-NC	945	-	3448	3696	1654	1120	-	-	-	1420	874
1W1A-CA	990	-	3448	3694	1684	1110	-	770	823	1420	873
1W2A-NC	940	519	3449	-	1654	1119	2110	-	-	1419	874
1W2A-CA	992	-	3448	3649	1640	1110	2110	769	833	1420	873
1W1B-NC	942	-	3444	3623	1650	1120	-	-	-	1440	-
1W1B-CA	1002	-	3451	3649	1652	1110	-	770	822	1449	874
1W2B-NC	989	581	3437	3623	1654	1116	-	-	-	1458	870
1W2B-CA	998	-	3442	3648	1652	1110	-	770	-	1422	873

The major vibrational bands identified for silicates are: v3 SiO_4^{4-} (asymmetric Si-O stretching), which is normally centred on 970 cm^{-1} (for C-S-H), v4 SiO_4^{4-} (out-of-plane Si-O bending), centred at 525 cm^{-1} and v2 SiO_4^{4-} (in-plane bending) centred at 458 cm^{-1} . Samples exposed to carbon dioxide showed an increase in plan for the v3 SiO_4^{4-} bands and a decrease in intensities of the v2 SiO_4^{4-} bands between 450-530 cm^{-1} . The carbonated waste samples showed flattened, deformed band for SiO_4^{4-} whereas non-carbonated W1 and W2 samples presented v3 SiO_4^{4-} band at about 940 cm^{-1} , indicating a lower degree of hydration than for carbonated analogues. Samples 1W1A and 1W2A (carbonated) also showed a band at about 820 cm^{-1} that is attributed to the silanol group, which is a silicon atom bounded to a hydroxyl group. This band was not present in the control sample and in the non-carbonated samples. Other major vibrational bands can be attributed to v3 CO_3^{2-} at 1420 - 1430 cm^{-1} and v2 CO_3^{2-} at 874 cm^{-1}. All samples presented bands at these frequencies, indicating that carbonation had taken place.

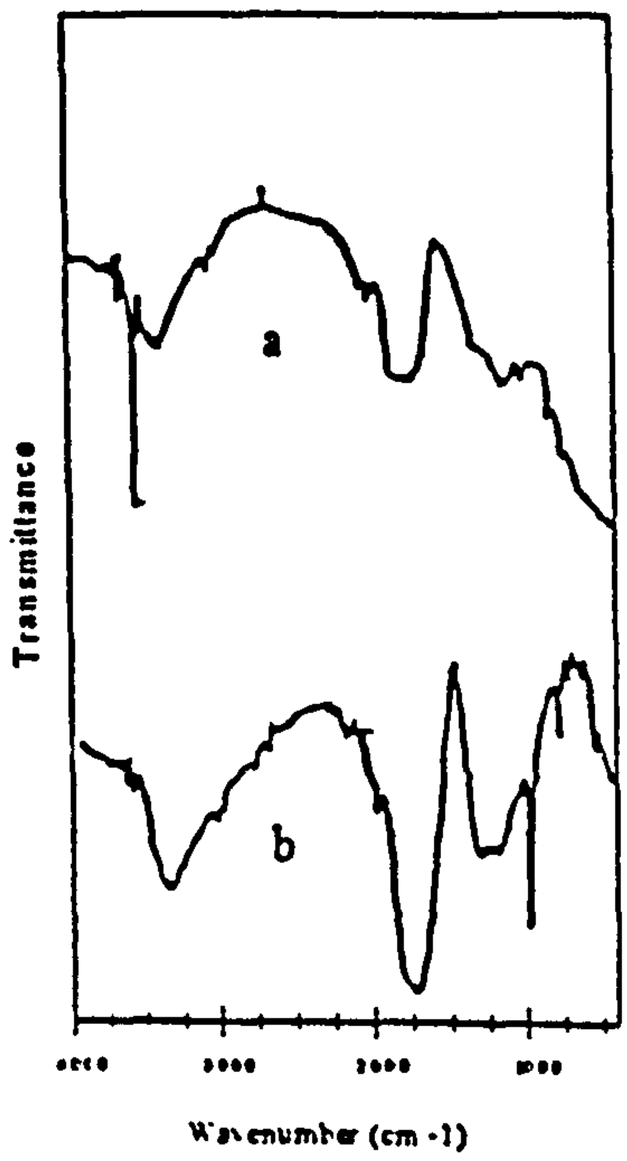


Figure 6.2: FTIR spectrum - a) Control non-carbonated; b) Control carbonated

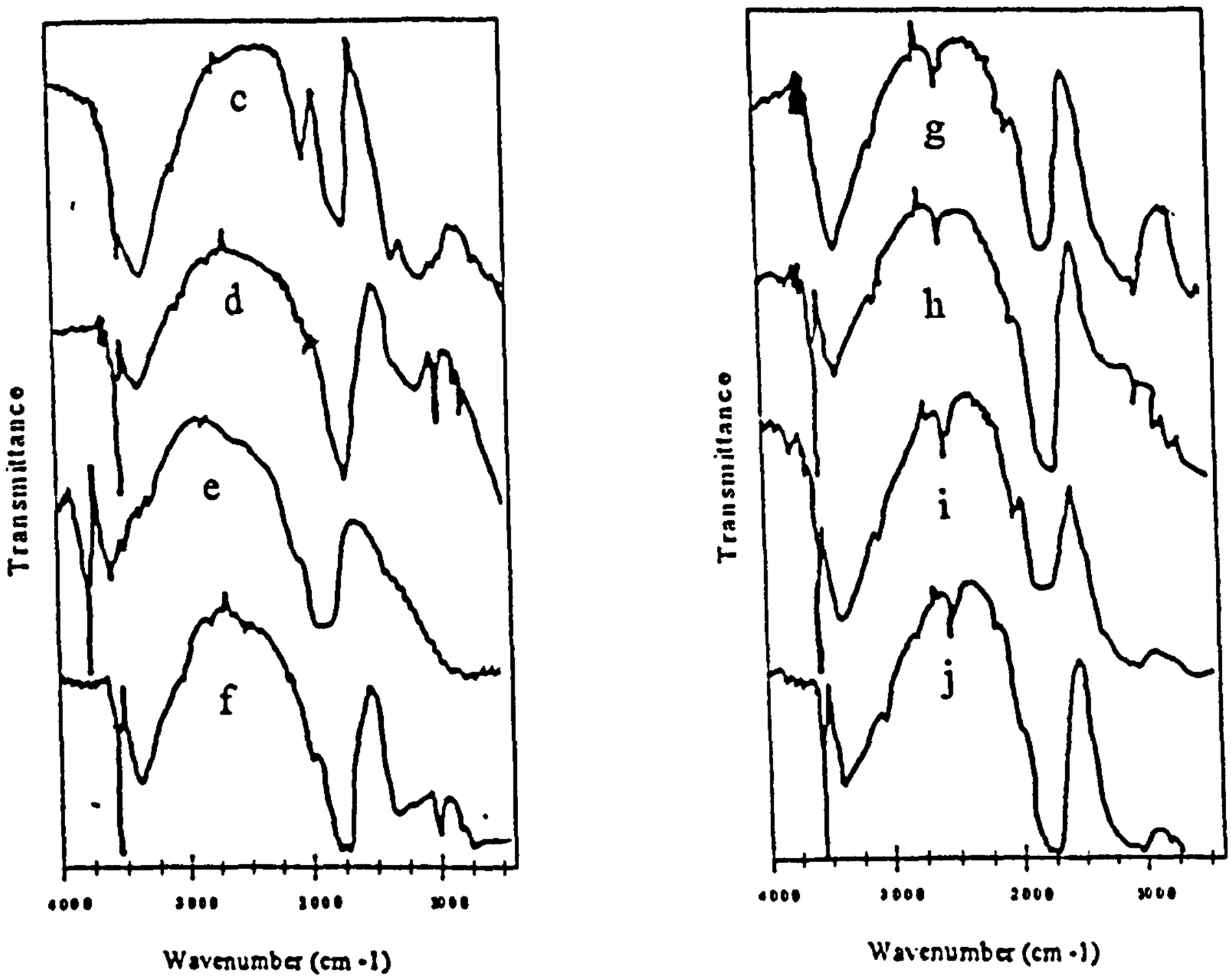


Figure 6.2: FTIR spectrum - c) sample 1W1A-non-carbonated; d) sample 1W1A-carbonated; e) sample 1W2A-non-carbonated; f) sample 1W2A-carbonated; g) sample 1W1B-non-carbonated; h) sample 1W1B-carbonated; i) sample 1W2B-non-carbonated; j) sample 1W2B-carbonated

For samples left in nitrogen the v3 CO_3^{2-} band was also evident due to the presence of carbonate ions in the waste material and also as a result of carbonation that might have occurred during sample preparation (Socrates, 1994).

In addition, vibrational bands were also identified at 1101-1157 cm^{-1} and are associated with v3 SO_4^{2-} . In samples 1W1A and 1W2A the SO_4^{2-} band occured around 1120 and 1119 cm^{-1} respectively, due to presence of ettringite and perhaps some monosulphate, which for the latter hydrate was obscured because of overlapping with SiO_4^{4-} . A shoulder at 1110 cm^{-1}, in sample 1W1A and 1W2A (carbonated), indicated the formation of gypsum. With respect to the carbonate band a proportion of the phase can be attributed to the decomposition of ettringite by CO_2 resulting in the formation of gypsum, calcite and alumina-gel. Alumina-gel was more difficult to detect by the FTIR, though a band was identified at 770 cm^{-1} possibly due to Al-O vibrations of aluminate mineral compounds in carbonated samples of 1W1A and 1W2A.

Other important bands such as the broad band near 3450 cm^{-1} was due to symmetric stretching of water (H-OH) while the one at 1640 cm^{-1} was assigned to v2 bending deformation mode of water. The sharp band appearing at 3640 cm^{-1} was due to asymmetric stretching vibration of OH groups as a result of surface bound hydroxides - $Ca(OH)_2$, Metal-OH, etc.

There was also a characteristic band at 2110 cm^{-1} in samples containing waste 2, arising from the CN^- stretch reflecting the high cyanide component of the waste. It can be clearly observed that the cyanide band remains unchanged after carbonation.

NMR Analysis

^{29}Si Solid State MAS NMR Spectra

^{29}Si MAS NMR spectra of samples control, 1W1A and 1W2A, carbonated and non-carbonated, are shown in Figure 6.3.

Under certain conditions solid state ^{29}Si MAS NMR spectra of hydrated cements and cement stabilised wastes can be used to quantify the extent of silicate polymerisation

(Hanna et al., 1995). The characteristic features of the ^{29}Si spectra of the cements are the chemical shifts of the various Q^n units (Thomas et al., 1993; Hanna et al., 1995). Resonances observed around -71, -78, -84, -93, and -105 ppm are due to Q^0, Q^1, Q^2, Q^3, and Q^4 Si environments respectively. The Q^3 environment may include a contribution from $Q^3(1Al)$ (Thomas et al., 1993). Hanna *et al.* defined a "degree of silicate condensation", *C*, as a percentage:

$$C = \frac{\sum nA(Q^n)}{4\sum A(Q^n)}$$

where $A(Q^n)$ is the area under each Q^n peak, and is obtained by spectral simulation. The individual resonances obtained for each sample by simulation are given in the Table 6.5. The intensities of the spinning sidebands were included in the total intensities given in Table 6.5 for the various Q^n species.

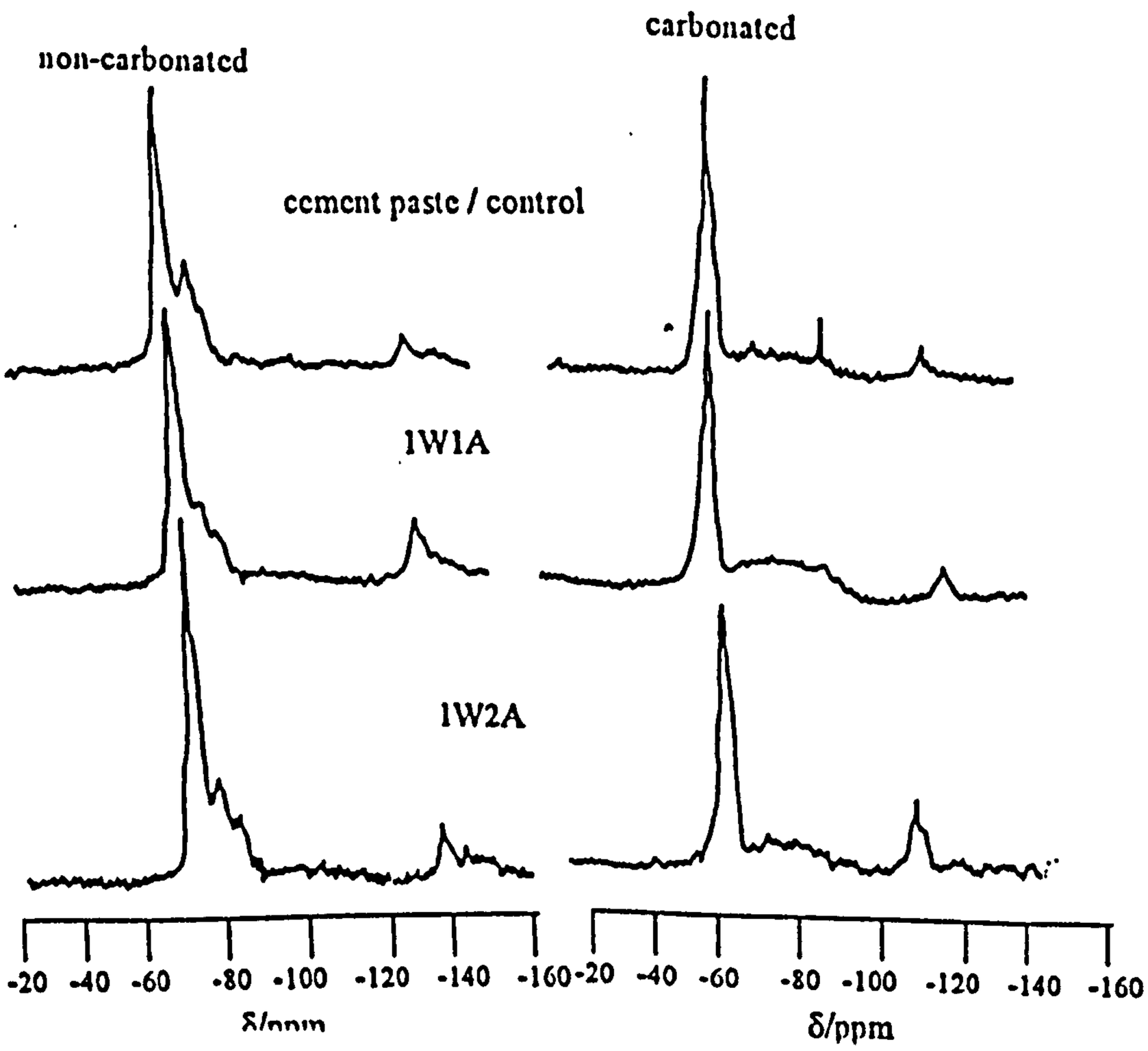


Figure 6.3: ^{29}Si MAS NMR analysis of carbonated and non-carbonated specimens

Table 6.5: Summary of ^{29}Si NMR results for non-carbonated and carbonated specimens

Samples	Position (δ)	Width (ppm)	%	% Condensation†
NC**				
Control - OPC	-78.8 - (Q^1)	31.9	15.6	14.5
	-71.2 - (Q^0)	1.1	4.8	
	-71.9 - (Q^0)	5.6	46.2	
	-79.2 - (Q^1)	4.4	24.5	
	-83.9 - (Q^2)	5.1	9.0	
1W1A	-64.7 - (Q^0)	6.2	1.2	15.2
	-71.5 - (Q^0)	4.8	51.1	
	-78.3 - (Q^1)	10.4	40.6	
	-85.0 - (Q^2)	3.0	1.2	
	-100.5 - (Q^3)	26.8	5.9	
1W2A	-66.3 - (Q^0)	12.0	5.4	14.8
	-72.7 - (Q^0)	5.7	35.8	
	-72.1 - (Q^0)	1.6	19.4	
	-79.8 - (Q^1)	5.3	25.8	
	-85.6 - (Q^2)	4.9	7.4	
	-103.8 - (Q^3)	24.0	6.2	
CA**				
Control - OPC	-63.8 - (Q^0)	15.2	6.7	24.8
	-70.2 - (Q^0)	4.9	61.3	
	-83.9 - (Q^2)	6.8	5.2	
	-93.3 - (Q^3)	10.4	16.4	
	-105.6 - (Q^4)	13.8	9.2	
	-106.2 - (Q^4)	0.8	0.6	
1W1A	-71.5 - (Q^0)	4.4	45.2	41.7
	-93.1 - (Q^3)	31.7	52.1	
	-109.4 - (Q^4)	8.1	2.7	
1W2A	-71.2 - (Q^0)	6.0	81.4	13.0
	-83.3 - (Q^2)	6.9	3.9	
	-93.1 - (Q^3)	18.5	14.7	

Note: * NC = non-carbonated and CA = carbonated

† = % condensation = $100 \times \Sigma\, n\, A(Q^n) / 4\, \Sigma\, A(Q^n)$

Most of the spectras were best fitted by assigning two peaks to the Q^0 region, both with chemical shifts in the region -70 to -72 ppm, but with very different widths. The appearance of the spectra allowed them to be placed into one of two groups, *viz* carbonated and the non-carbonated specimens.

There are several observations to be made from the data in the Table 6.5:

a) the first concerns the comparison of the non-carbonated sample without (control) and with (1W1A and 1W2A) the addition of the metallic waste. The values for the % condensation (*C*) are little affected by the presence of the waste.

b) this observation does not hold for the carbonated cement pastes. Carbonated OPC/control shows a reduction in the % condensation in the presence of the W2 (sample 1W2A), whereas for W1 (sample 1W1A) the presence of the waste resulted in a marked increase in the extent of condensation.

c) for all samples, except 1W2A, carbonation results in significant increases in the % of condensation.

^{27}Al Solid State MAS NMR Spectra

The principal features of the ^{27}Al MAS NMR spectra of calcium aluminate phases in cements have been described by Skibsted *et al.*[4] Tetrahedrally coordinated Al gives resonances in the region 50 to 80 ppm, while resonances from octahedral Al are in the region -20 to +20 ppm. In the octahedral region ettringite gives rise to a characteristic resonance at 13.1 ppm and the monosulphate phase C_4ASH_{12} at 11.8 ppm. Figure 6.4 gives the spectra of the samples.

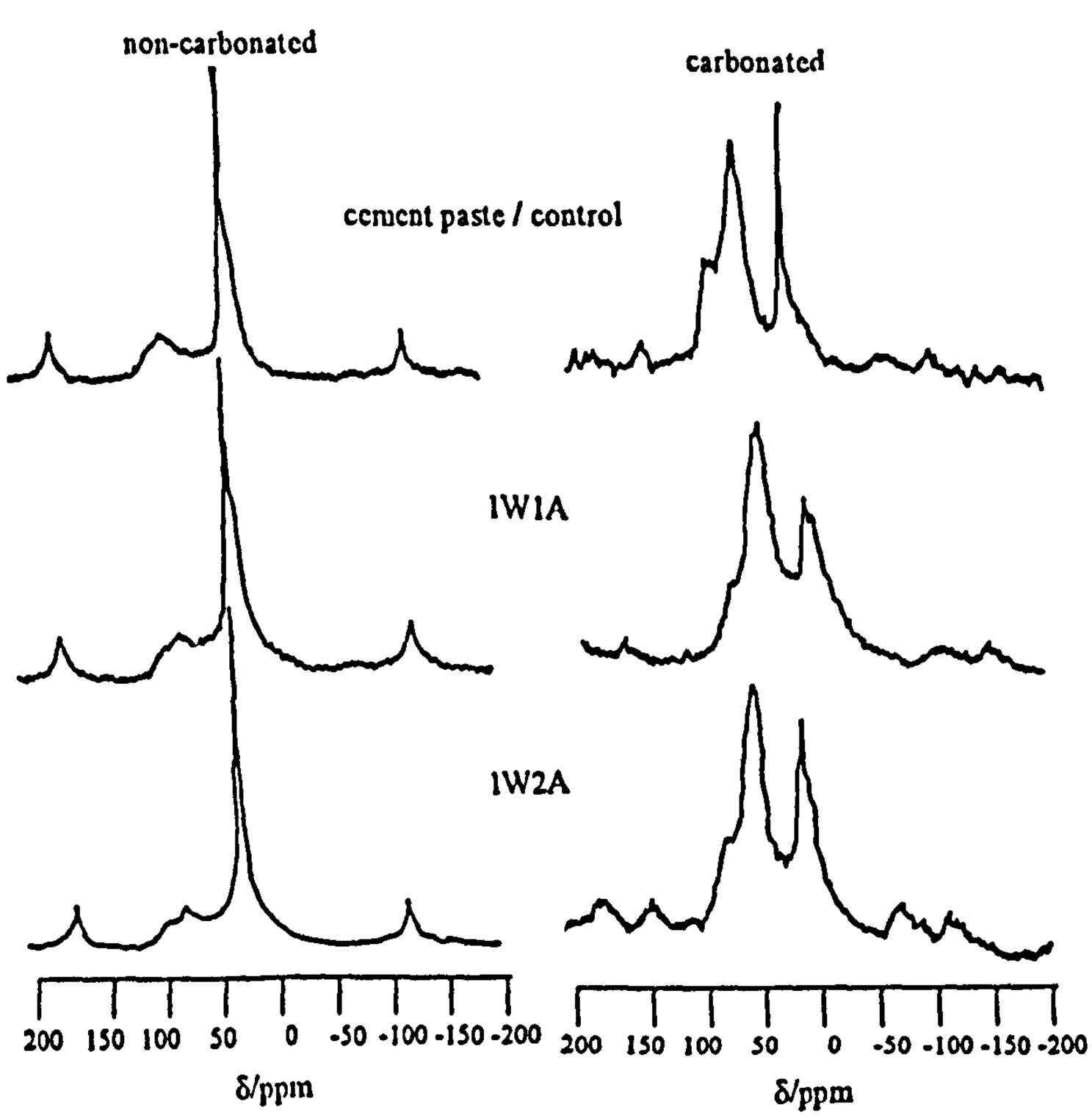


Figure 6.4: ^{27}Al MAS NMR analysis of the carbonated and non-carbonated specimens

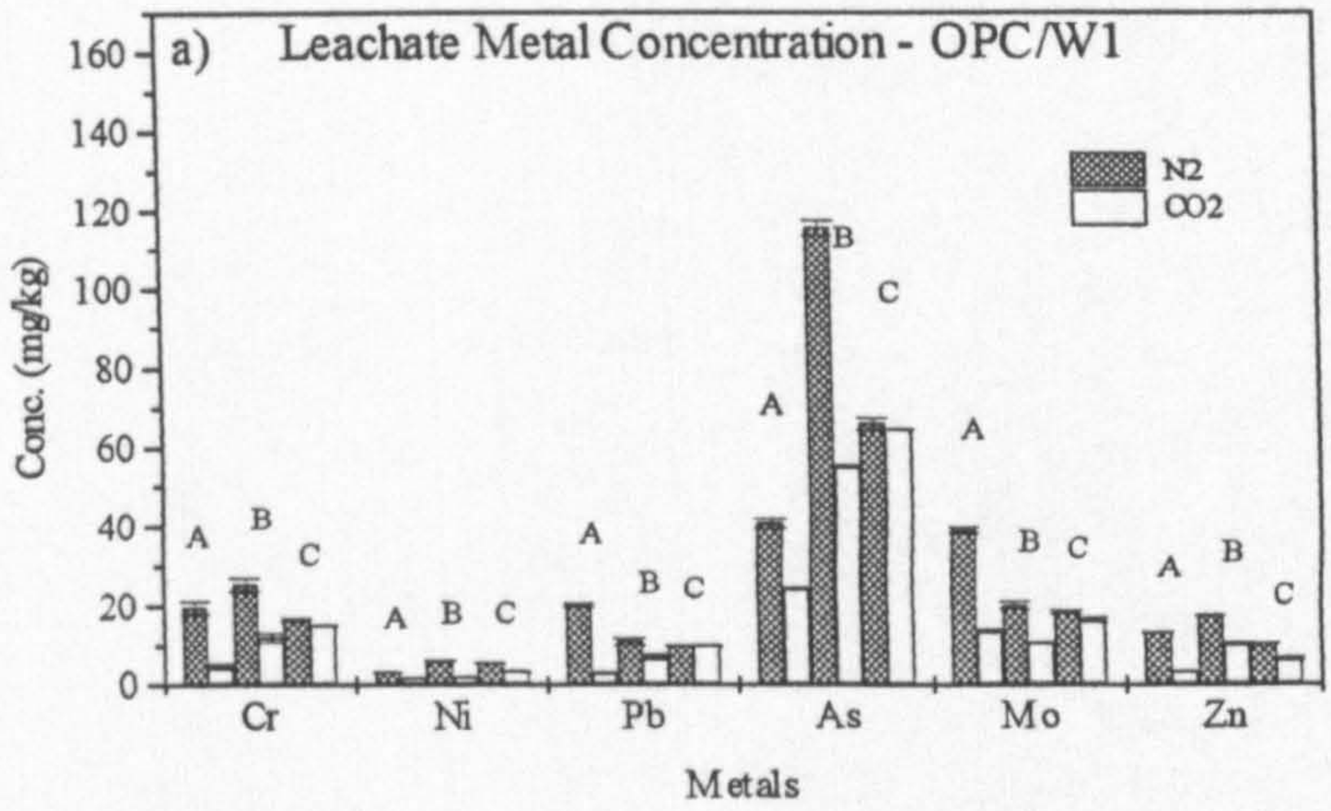
The spectra of the control non-carbonated sample was dominated by a relatively sharp ettringite-like signal at about 13.0 ppm, with a low frequency and broader shoulder which was probably due to the presence of monosulphate phase. There was also a broad signal with a peak maximum around 65 to 68 ppm due to tetrahedral aluminium, with a shift which is similar to that measured by Skibsted *et al.*[4] for the calcium aluminate phase CA_2. The control carbonated sample showed enhanced tetrahedral Al signals that dominate the spectra. A higher frequency shoulder appeared at *ca.* 80 ppm for the tetrahedral resonance and on the basis of the chemical shift this was possibly due to CA or C_3A (Skibsted et al., 1993).

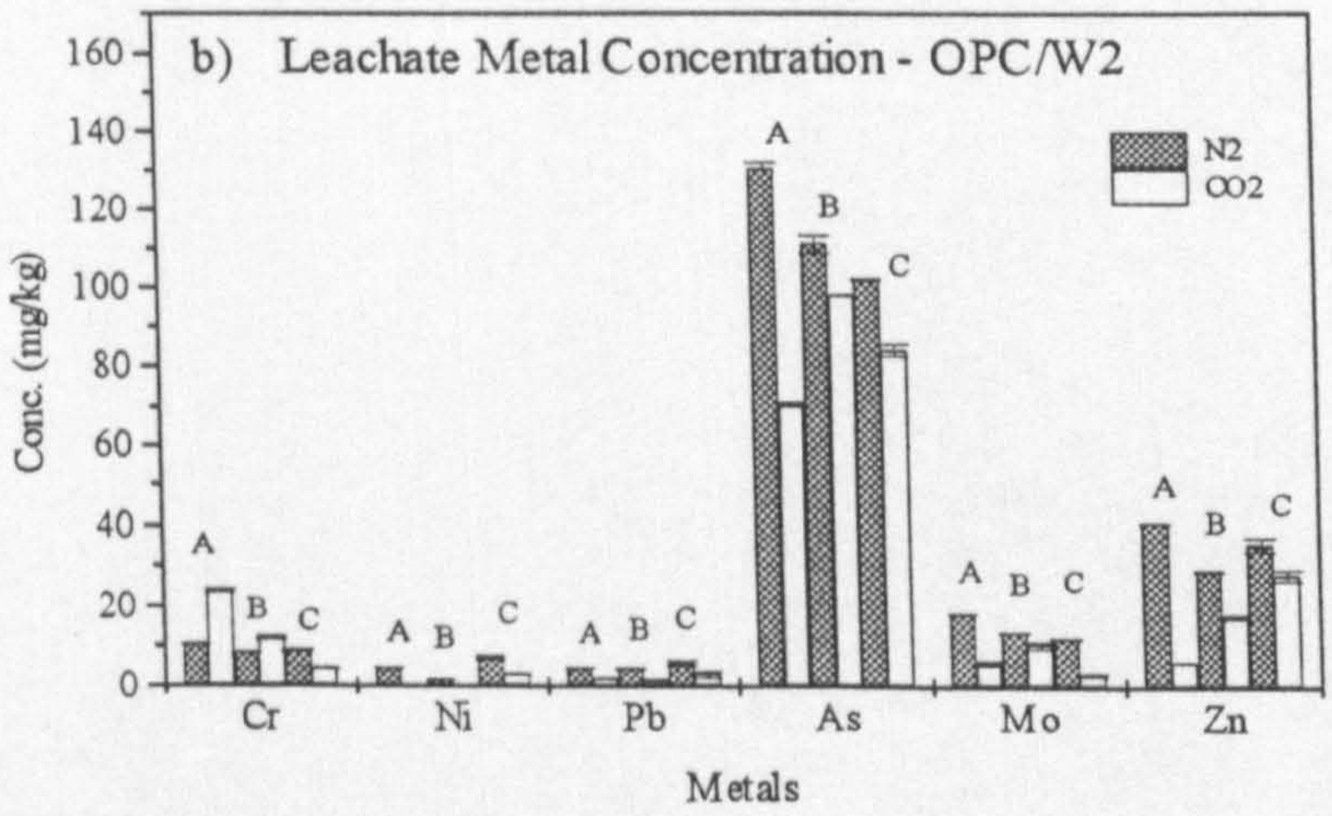
The introduction of metallic waste into the non-carbonated sample did not significantly change the relative intensities of the tetrahedral and octahedral resonances, but there was a reduction in the intensity of the shoulder which was assigned to monosulphate. In addition the high frequency shoulder at *ca.* 80 ppm appeared as a tetrahedral resonance in samples 1W1A and 1W2A.

Much broader spectra resulted from the introduction of metallic waste into the carbonated cement pastes. Sample 1W2A showed a moderate increase for the AlO_4 resonance in the presence of the waste when compared to control, but the spectra of sample 1W1A indicate a significant increase in the AlO_4 resonance.

6.3.3 Leaching Characteristics

Figure 6.5a-f shows the concentration of the metals: Cr, Ni, Pb, As, Mo and Zn determined in leachates from different samples. The pH values after 24 hours extraction recorded for samples cured in carbon dioxide and nitrogen were between 8 to 10 and 10.5 to 11.5, respectively.





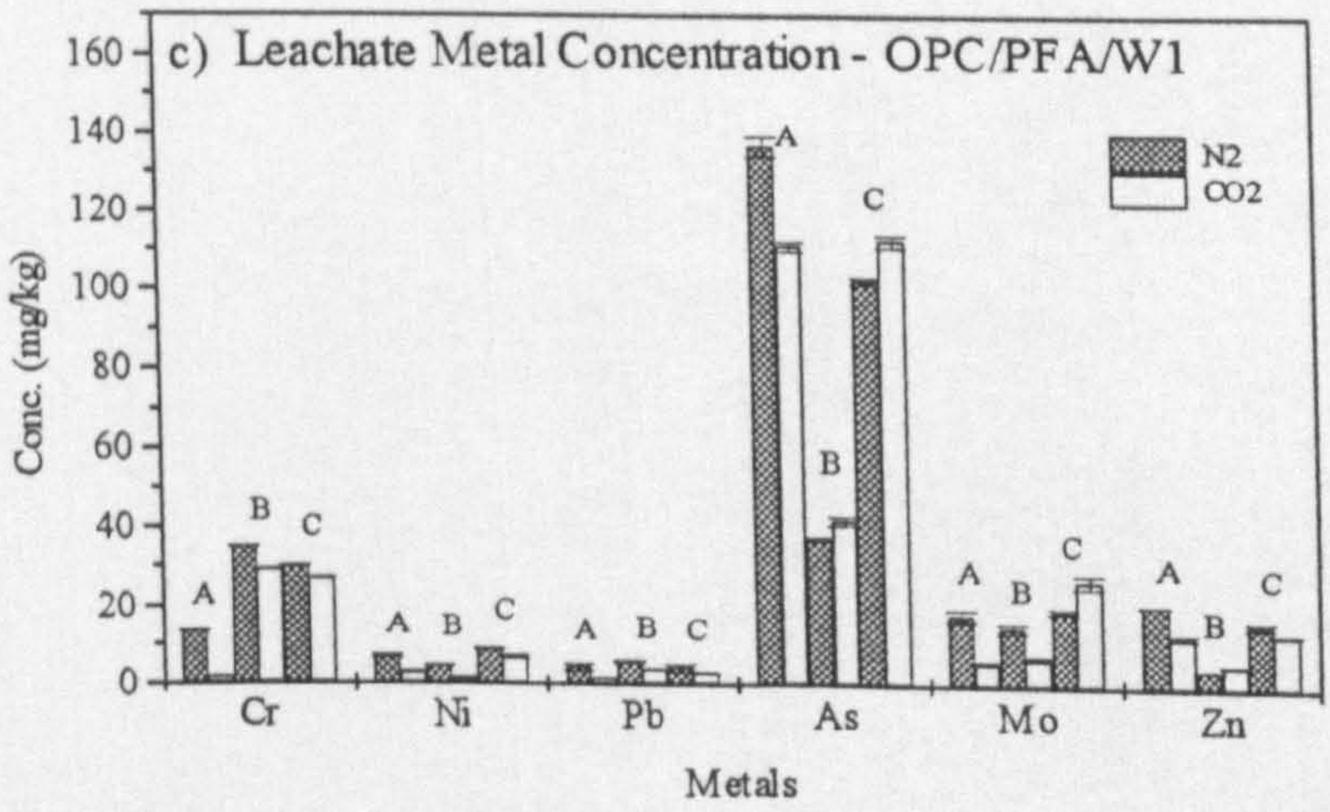
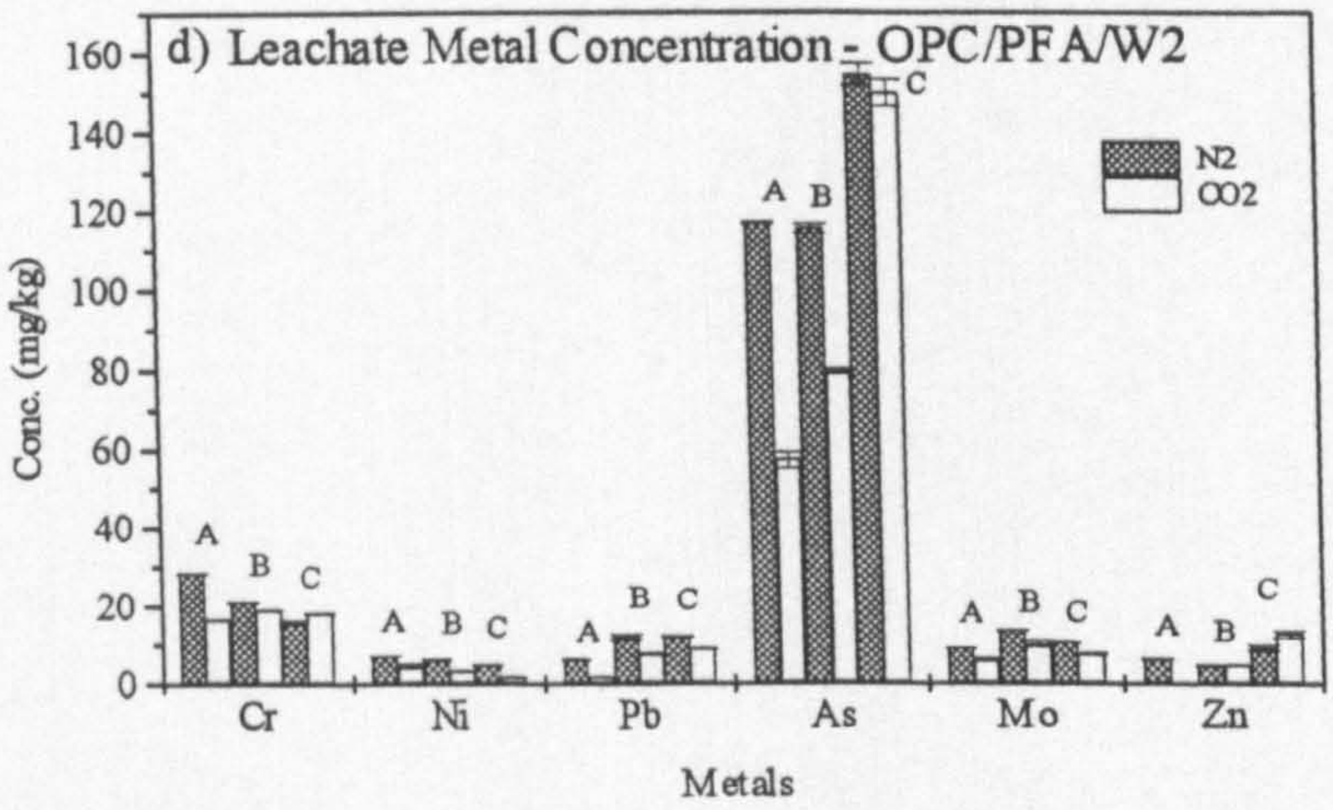
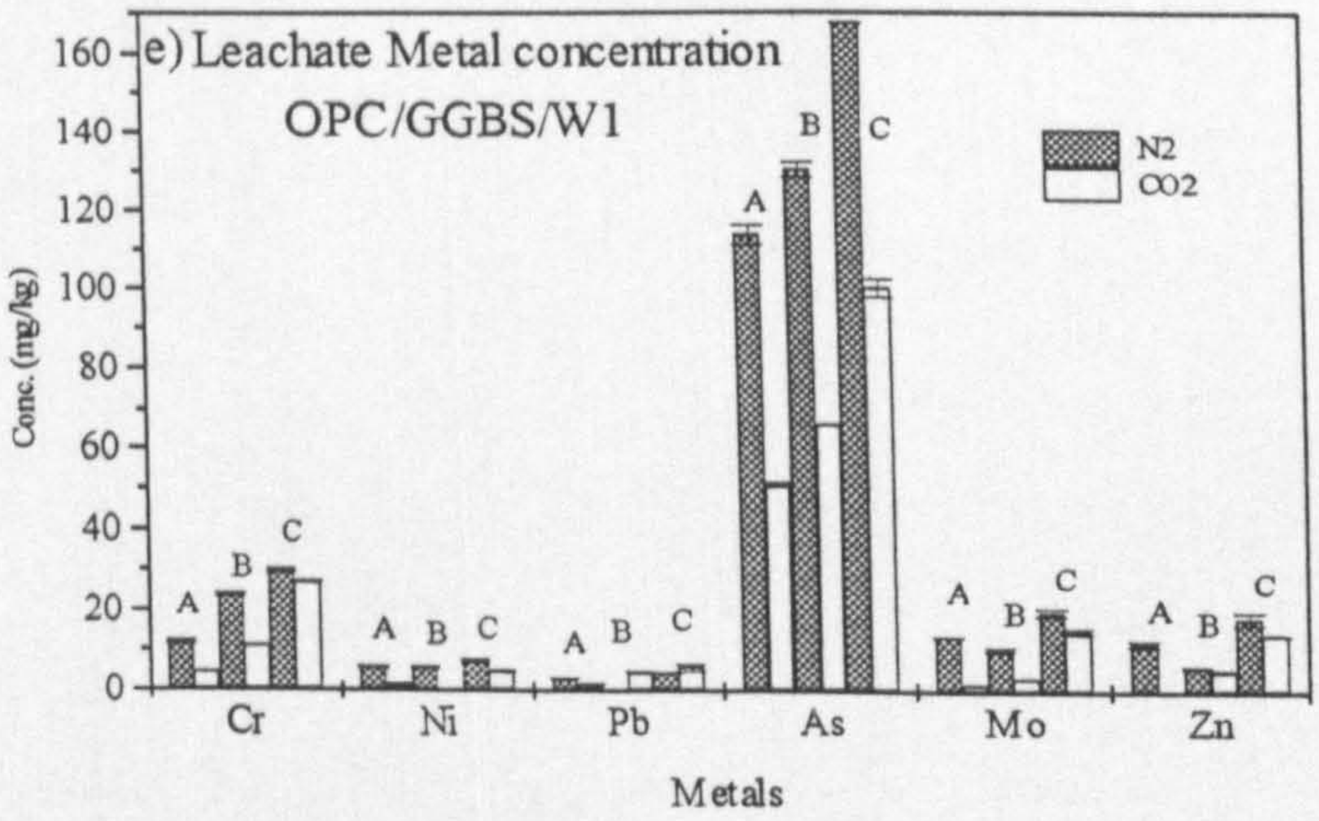


Figure 6.5a-c: Leaching characteristics





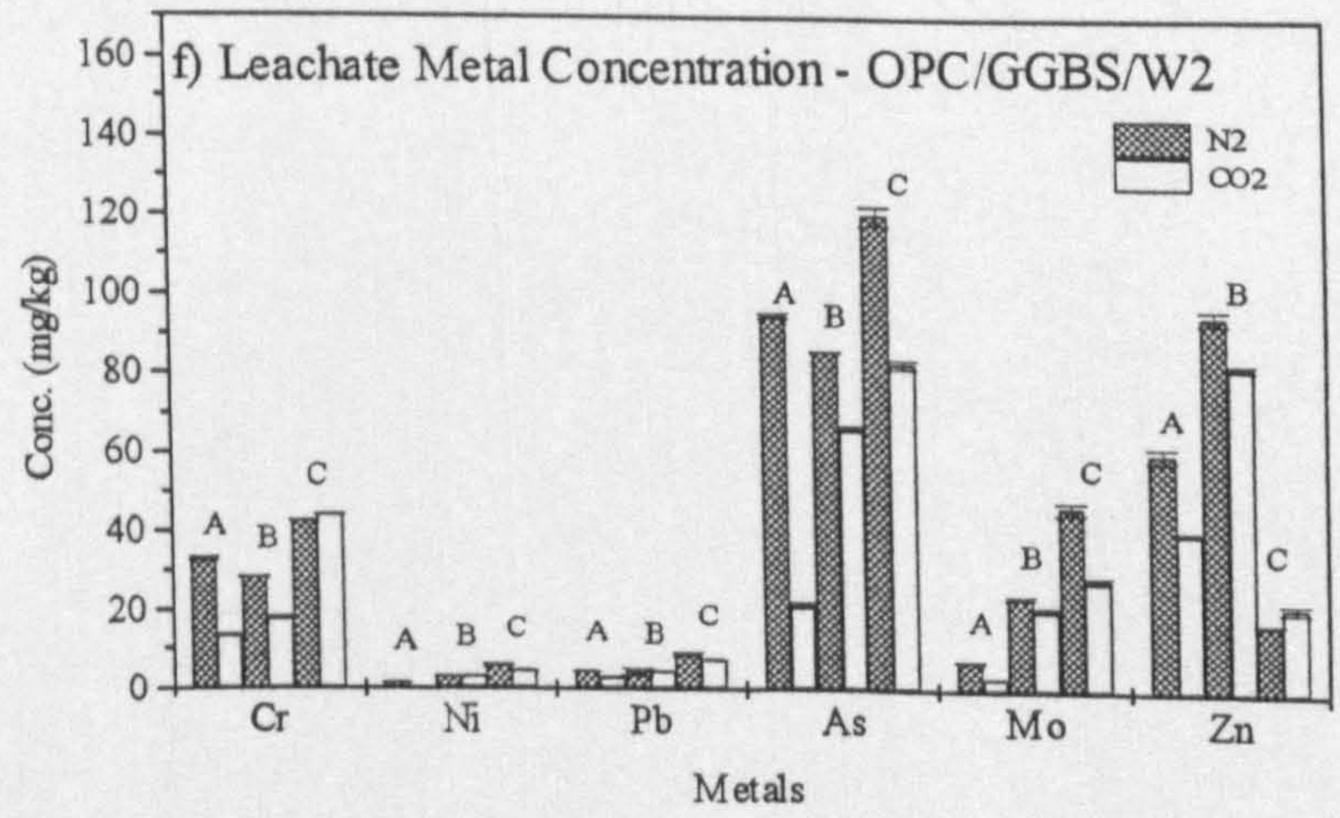


Figure 6.5d-f: Leaching characteristics

In general, the carbonated waste forms retained metals better than nitrogen cured specimens. Nevertheless, it is important to note the effect of binder types on leaching characteristics, for example, by the addition of PFA and GGBS increased leachable metal concentration for metals such as As and Cr up to 16% when compared to OPC only -waste mixes. For metals such as Zn, Pb and Ni a significant reduction of up to 85% for Zn and Pb, and 61% for Ni was recorded for sample 1W1A, despite pH being near the minimum solubility for those metals. An average reduction in leachate metals content for (A) of 30 to 45% was observed when compared to mixes B and C indicating that waste forms solidified and carbonated with carefully chosen binder mix designs, may be used to improve metals fixation.

It is important to note that the results also indicate that for some mixes cured in nitrogen, leaching properties were improved as a result of stabilising waste with OPC. For W2, for some mix designs, leachate metals content were lower for certain metals for the nitrogen cure showing that carbonation may not always be appropriate.

6.4 DISCUSSION

Carbonation appears to be associated with improved waste form mechanical and chemical characteristics.

Carbonation affects the microstructural development of waste forms primarily through the precipitation of calcite in porosity, which in turn influences the fixation of toxic metal species. Furthermore, evidence is produced to suggest that the process of carbonation can be optimised under controlled conditions to significantly improved leachate performance.

The effect of carbonation on strength development is marked. A clear relationship between calcite development and strength development can be demonstrated (Figure 6.6). This relationship suggests that the amount of calcite generated has a direct effect on strength distribution. It is also interesting to note that samples with very low w/s ratio

or high cement content do not necessarily have the highest strength values. The mix designs that promote a maximum uptake of carbon dioxide have higher strength values and , as it will be discussed below, enhanced calcite contents and an improvement in metals fixation.

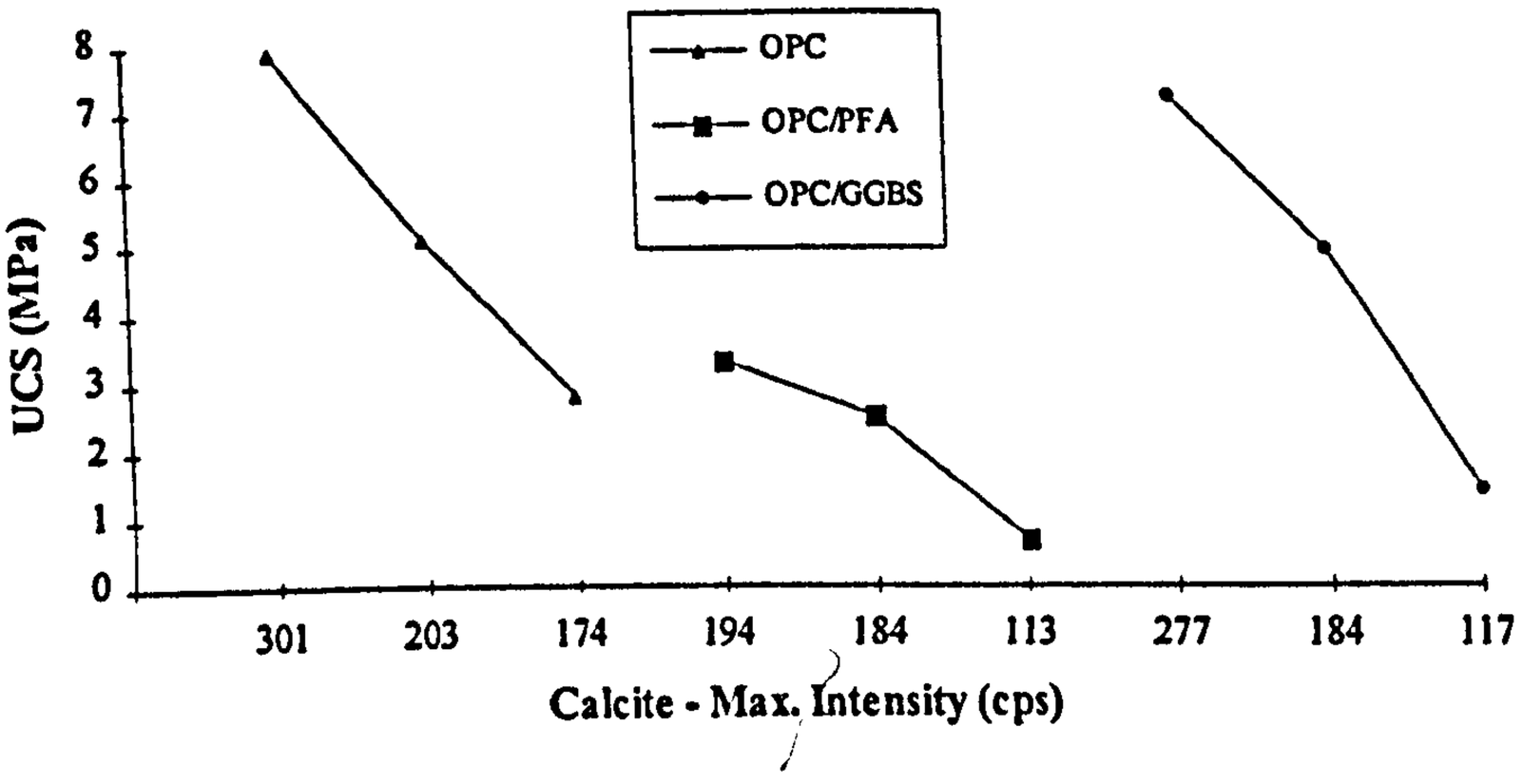


Figure 6.6: Relationship between calcite content and strength development

The mineralogy of samples appears to be very dependent of the presence of carbon dioxide, the type of binder and the amount of waste used. The presence of metals containing waste is responsible for increased calcium carbonate contents, compared to control samples and may this be due, in part, to the precipitation of some of the cations as carbonate species, demanding a constant presence of Ca^{++} ions, which are provided by the unhydrated cement. This result in an acceleration of the hydration of C_3S and a polymerisation of the silicate structures, within hydration rims, as previously shown.

Ettringite is not normally found in carbonated waste forms as it decomposes to form gypsum and calcite (Nishikawa et al., 1992). Vaterite was the calcium carbonate polymorph present in some samples that contained GGBS. Although it is usually a metastable compound at ordinary temperature and pressure, the rapid initial carbonation reaction rate combined with the consequent high amount of heat produced during the reaction with cement and non-hydraulic slag might be the cause for its formation in this case (Bukowski et al., 1979).

XRD and SEM studies have shown that the structure of individual calcite crystallites are generally very small (<3mm) and are uniformly dispersed throughout the waste forms porosity. Factors such as the polymerisation of silicates, particularly within hydrated cement grains and the presence of both silica and metals in the carbonate phases could influence the size and crystallinity of this phase. In addition, as carbonation reaction is very rapid and exothermic, and this may also influence morphology of this phase.

The vibrational frequencies measured by FTIR were associated with changes in the hydrated cement phases which could be used to differentiate between amorphic and crystal forms, whether normal cement hydration or carbonation induced phases have taken place. It was not evident though, the difference between samples carbonated under optimised conditions (A) and when it was not the case (B and C). However, important information regarding the effects of carbonation upon the cement-solidified waste forms was obtained. For example, samples exposed to the accelerated carbonation regime showed an increase in plan for the the $\nu 3$ SiO_4^{4-} bands and a decrease in intensities of the $\nu 2$ SiO_4^{4-} bands between 450-530 cm^{-1} , confirming polymerisation of the orthosilicate units and an acceleration of the hydration of C_3S to form C-S-H.

The general tendency with silicate structures is that the greater the degree of condensation the higher the wavenumbers at which absorption occurs. Also, the bands are deformed to a greater extent as a result of the complexity of the interactions within the crystal lattice (Bensted et al., 1974a). Substitution of various ions in the alite lattice reduces the sharpness or even causes disappearance of some silicate bands and broadening of bands. The indication of the presence of silanol groups in some of the

carbonated samples could be used to identify a possible mechanism for metal fixation in the carbonated matrix. Metal silicates are nonstoichiometric compounds in which the metal is coordinated to silanol groups, SiOH, in an amorphous silica matrix (Conner, 1990).

Another important observation is that the asymetric stretching vibration of OH (3640 cm^{-1}) can be a result of the surface bonding of hydroxides $Ca(OH)_2$, metal-OH, etc. This peak is useful for diagnosis of the initiation of C_3S/C_2S hydration. For example, the lack of sharp peak in sample 1W1A (non-carbonated) could indicate a retardation of the hydration of alite due to the addition of the waste. Also the presence of hydroxyl band on the carbonated waste/OPC systems may be unexpected as $Ca(OH)_2$ is normally consumed during carbonation. However, the industrial wastes were pre-treated with NaOH/KOH, which could account for the presence of this band.

^{29}Si NMR unambiguously quantifies the extent of silicate polymerisation, which is dramatically increased for all carbonated samples. First, signal enhancements occur in the range between -83 and -100 ppm, indicating the introduction of silanol groups to Q^2 and Q^3 units and along with it the degree of polymerisation is increased by the presence of Q^4 units (Thomas et al., 1993). The amount of Q^0 reported was also significant. Normally Q^0 is the sign of an incomplete hydration of the original calcium silicate phases. This could be due to the retardation effects of the metals upon the cement paste, for the non-carbonated samples. For the carbonated samples, this could be due to the initial acceleration of hydration of the clinker grains, by the presence of carbon dioxide, forming silicate rich compounds (decalcified silica gel - Q^3 and Q^4 species), being the reaction limited by water content.

For carbonated samples additional resonance appears near -93 ppm, this is assigned to Q^3 (1Al) (Thomas et al., 1993). This resonance is distinct from the resonances at -99 to -102 ppm, which were assigned to Q^3. Thomas et al. suggested that this could be due to a cross-linkage between silicate and aluminate species. Additional support is given by the ^{27}Al MAS NMR data, which propose that upon carbonation, octahedrally coordinated Al formed in the hydration process is converted back to tetrahedral Al, with the formation

of a mixed AlO_4/SiO_4 three dimensional network structure. However, it should be pointed out that there is considerable overlap between the shifts for variously substituted SiO_4 tetrahedra (Engelhardt et al., 1987) and the distinction made by Thomas et al. between Q^3 and Q^3 (1Al) ^{29}Si shifts may not be sound. Also, FTIR results suggested the presence of an aluminium hydrate gel, such as gibbsite, which will appear as an octahedral coordinated Al.

An analysis of leachates showed that a reduction in metal concentration was realised for carbonated samples compared to other mixes. Samples where the total carbon dioxide uptake were higher had higher calcite contents and gave the lowest leachate metal concentration for metals, such as Pb, Zn and Ni inspite of the effect of carbonation on the pH of the leachate solutions. This suggests that some metals precipitated as carbonates and may explain unidentified peaks that were apparent in the diffractograms obtained by XRD, in addition to modification of pore structure.

6.5 SUMMARY AND CONCLUSIONS

In this Chapter samples prepared using mix designs correspondent to the different degrees of carbonation zones, as previously determined, were investigated for their physico-chemical properties.

It is concluded that large amounts of calcite were characteristic of carbonated samples, as revealed by X-RD and FTIR techniques. Calcite content appears to be directly linked with the development of strength and enhanced metals fixation. Infrared and NMR spectroscopy indicated that accelerated carbonation has significant influence on the hydration of the waste forms by increasing the degree of polymerisation of the silicate units, with a consequent acceleration of the hydration of the cement paste. This negates the normal retardation effects of metals such as Pb. Also the reactive silanol groups were identified in some samples containing industrial wastes, suggesting possible metal fixation mechanism. This point will be further discussed in Chapter 7.

SEM analysis also confirmed that an acceleration of alite hydration occurred, with a de-calcification of hydrated rims of cement grain (Si-rich) and dense calcite precipitate infilled porosity. Some metals appeared to be preferentially incorporated in silica rich rims as in the calcite infilling porosity. Micro-cracking was also observed and this may be the result of thermal stresses caused from the heat generated by the rapid rate of the reaction with CO_2 during accelerated hydration.

The importance of controlling carbonation has shown to be essential in order to obtain enhanced chemical and physical qualities of the solidified waste forms. Despite the complexity of the industrial wastes, the results have indicated an association between metals, calcite precipitates and silica-rich C-S-H structures, although it is still rather difficult to predict the actual nature of chemical association from these results alone. Therefore, an investigation with single metal solutions (laboratory prepared) would be necessary to help in further elucidate the carbonation reaction with the doped cement systems, and this will be the subject of the following Chapter.

CHAPTER 7

CARBONATION OF CEMENT-BASED SYSTEMS DOPED WITH SINGLE METAL SOLUTIONS

7.1 PREVIEW

The preceding Chapter examined the physico-chemical properties of solidified hazardous waste materials carbonated under controlled conditions, and showed that it is possible to significantly improve the immobilisation of certain metals. The previous Chapters however, have elucidated the effects of carbonation on complex industrial waste systems bound by cement.

The objective of this Chapter is to investigate simple waste systems whereby cement is doped with single metal solution to enable a better understanding of the effect of carbonation on hydrated cement paste containing specific metals to be developed.

Four metals known to be toxic have been chosen for closer examination in this Chapter. They are: cadmium, lead, nickel and zinc, added as single metal solutions, and are carbonated to enable the individual effects of each metal selected to be studied. The sources of metals and their properties, particularly those relevant to the solidification process are described prior to presentation of the experimental details which includes microstructural characterisation and an examination of leachate metal content. The Chapter concludes with a discussion and summary of the main points.

7.2 GENERAL BACKGROUND

The two industrial wastes studied previously were composed of a range of heavy metals hydroxides, and were received as filter cakes after precipitation with lime or another alkali. They were of low solubility and had a pH ranging between 6 and 8. These materials have shown to be of a very complex composition, and normally subjected to complex treatment methods, as already discussed in Chapter 1.

At present, a large number of investigations have been conducted on the physical properties of cement paste doped with individual metal solutions. Hills (1993) has studied the interference effects of different anions combined with metals based on heat of hydration evolved. However, most of the studies have investigated the effects of metallic compounds as nitrates, and found that when metal is present in small amounts cement hydration is accelerated, but at higher concentration (>4%) zinc, lead, copper, cadmium, mercury, nickel retard setting (Thomas et al., 1981; Cocke et al., 1989; Cartledge et al., 1990; Balzamo et al., 1992; Bhatty et al., 1993; Tumidajski et al., 1994). A common explanation for these effects is the precipitation of insoluble metal colloidal gel on the cement grain surfaces, which prevents further hydration.

Bonen et al. (1994 and 1995) have drawn the attention to the interaction of the heavy metals when introduced as nitrates and oxides. They supported the idea that when metals are incorporated as salts, they may undergo hydrolysis, resulting in lowering the pH and the CH content of the paste.

$$M^{n+} + nH_2O \leftrightarrow M(OH)_n + nH^+ \qquad \text{(Eq. 7.1)}$$

In contrast, heavy metal oxides have lower solubilities in the alkaline pore solution of the cement paste and consequently could be more suitable for microscopial examination.

Nevertheless, waste metal solutions can be precipitated as the species of choice, and this can be advantageous where studies of fixation mechanisms are concerned. However, the solubility of the species produced will depend to some extent on other species present in solution, but a solution system can be optimised in any case.

7.2.1 General Properties of the Metals Examined

Cadmium

Cadmium is a Group IIB element with only one oxidation state, that of +2. Cadmium and its compounds are highly toxic. Chronic poisoning can be induced by as for example, a outbreak of Itai-Itai disease in Japan. Cadmium may also be a carcinogen.

The main industrial source is from electroplating particularly the cadmium cyanide complex. Other cadmium wastes include textile printing, mine drainage, battery manufacture, and some photographic waste (Patterson, 1985; Conner, 1990).

Treatment methods include precipitation as hydroxide, sulphide or carbonate. Recovery is also possible. Freshly precipitated cadmium hydroxide reportedly leaves approximately 1 mg/L in solution at pH 8.0, but only 0.1 mg/L at pH 10.0 (Sittig, 1973). In the presence of complexing agents, for example cyanide, the cadmium ion will not precipitate and once again pre-treatment is necessary. The carbonate precipitate will form at a pH between 7.0 - 8.0. Between pH 8.0 - 11.0, about 99% of the cadmium will be speciated as the solid carbonate. Above pH 9.0 the relative proportion of cadmium speciated as hydroxide begins to rise until the system is primarily hydroxide above pH 11.0.

Cadmium can be fixed using cement-based solidification technology so long as the pH remains high. However, if a leachant pH falls below about 7.0, cadmium is soluble in high amount levels. Shively et al. (1986) has demonstrated this pH effect for cadmium using a sequential batch leaching test which eventually neutralised the alkalinity of a Portland cement system. When waste forms containing cadmium are subjected to a diffusion-controlled leaching test scenario with neutral water as the leachant, cadmium leaching is very low. Cote et al. (1984) found only 0.008% of cadmium leached from a cement/PFA waste form after 11 months in such a system. Cadmium appears to be more pH sensitive than most of other metals.

Lead

Lead is a member of Group IVA of the periodic table. It has two valence states, +2 and +4, with the +2 state being the most common. Pb^{+4} compounds are regarded as being covalent, while Pb^{+2} compounds are primarily ionic. Lead is amphoteric and forms anionic plumbites and plumbates as well as both cations.

Lead occurs as many different minerals, for example, cerrusite ($PbCO_3$). The solubilities of these minerals are shown diagrammatically in Figure 7.1.

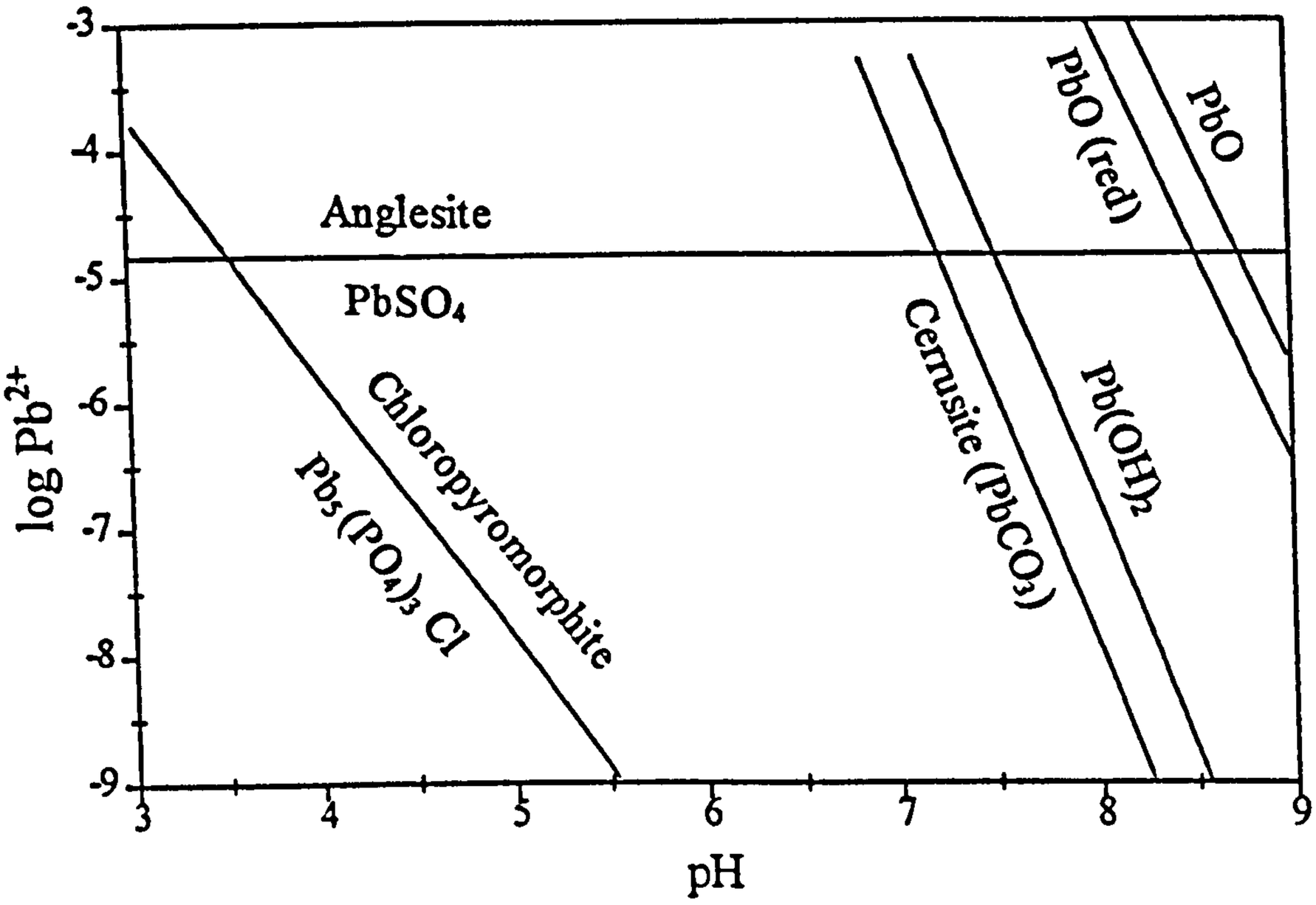


Figure 7.1: Solubility of lead minerals in the presence of CO_2 gas at 0.003 atmospheres (after Conner, 1990)

Lead and its compounds are cumulative poisons. Because of its long industrial and consumer use history, more is know about lead poisoning than about any other metal.

The primary uses of lead and lead compounds are in storage batteries, the manufacture of tetraethyllead, pigments, ammunition, solders, plumbing, cable covering, bearings, and caulking (Conner, 1990).

In general, the chemistry of inorganic lead compounds is similar to that of the alkaline earth elements (Kirk-Othmer, 1979). Many inorganic lead compounds possess two or more crystalline forms whose properties are different. Pb^{+2} forms a soluble nitrate, chlorate and acetate, and a low-solubility sulphate, carbonate, chromate, phosphate, molybdate and sulphide. It also forms complex mixed salts such as $2PbCO_3.Pb(OH)_2$. It is possible to say that lead is the most common and widespread problem encountered in metal fixation technology. Its pervasive presence and the many species in which it appears can make each waste type a technical challenge.

Nickel

Nickel is a Group VIII transition element and shows oxidation states -1, 0,+1, +2, +3 and +4. The +2 state however, represents the majority of all Nickel compounds (Conner, 1990). Nickel and its compounds are inhalation hazards, and may also cause allergic dermatitis. Some nickel compounds are even regarded as carcinogenic via ingestion.

The largest source of nickel commonly arises from plating industries, alloying, ceramics and printing industries (Patterson, 1985). Electroplating is by far the largest generator of nickel bearing wastes, indeed the waste from the pickling and plating industries pose a far greater problem than any other metal contaminant simply due to the wide spectrum of nickel alloys and the variety of pickling liquors used.

The presence of complexing agents can mean that high concentrations of this soluble nickel complex are found in treated waste waters.

The precipitation of nickel hydroxide from nickel bearing waste is the most common method of removal. Precipitation with carbonate is also common. $Ni(OH)_2$ has its lowest solubility at pH 10.0.

Leach test results for various solidification treatment systems show that there is usually no difficulty in fixing nickel to prescribed levels provided that the pH has been controlled. Simple nickel complexes may be treated by either oxidation/reduction using chemicals such as potassium permanganate, hydrogen peroxyde, iron, etc., but more sophisticated plating formulations may require sodium borohydride or hypochloride at elevated temperatures. The former is expensive, and the latter may oxidise chromium to +6 and thus than cause additional problems. It is advisable therefore to destroy all nickel complexes before treating the waste water (Conner, 1990).

Zinc

Zinc is a Group IIb element and its most common valence state is +2. Zinc is an important nutrient in plant and animal life, it is not toxic to humans, except when present in high levels.

The main industrial waste sources of zinc are from galvanising steel works, metal plating, inorganic pigments, paper production and zinc and brass metal works. Acid baths and rinse waters being the discharging source.

Most information on zinc fixation comes from the waste water treatment industry. Again, pH control with time is the most common treatment method, but ion exchange and evaporative recovery are common when the metal concentration is high enough. The problem occurs of cyanide or ammonia complexation of zinc are problematic and their removal before treatment is usually required.

The optimum range for zinc precipitation is between 9.0 - 9.8 (Conner, 1990) and $Zn(OH)_2$ experiences its lowest solubility at pH 9.2. In solidification systems, zinc is found to be strongly fixed by the tricalcium silicate component of Portland cement (Bhatty, 1987).

7.3 MATERIALS AND EXPERIMENTAL METHODS

OPC, the most common binder used in cement-based solidification, was chosen to prepare all solidified samples, as described in Chapter 2. The standard w/c ratio used was 0.3. This w/c ratio was found to be the most appropriate for the complete carbonation of the samples. The metals used as nitrates, were added at 1%, 5% and 10% by weight based on the cation. Chemicals with analytical reagent grade and distilled water were used throughout.

The doped-OPC samples were prepared by slowly adding the solutions to the cement while mixing thoroughly. Six samples were prepared for each doped cement and put into 32 mm x 32 mm PVC moulds. Half of the samples were cured in nitrogen environment and the other half were submitted to an accelerated carbonation regime as described in Chapter 6, for 1 hour. After 1 hour samples were removed to ambient (laboratory) condition (T = 22°C± 2 and Rh = 58%±5). Control specimens (OPC only) were also prepared and cured under both regimes. After 28 days ± 2 days the samples were tested for leachate composition and phase development. The methods used in this Chapter were described in Chapter 2.

7.4 RESULTS

7.4.1 Microcharacterisation Tests

Phase Development

The phase distribution within the OPC-doped cement samples may be seen by a comparison of the principal diffraction lines for each set of samples. Table 7.1 summarises the obtained data, where the relative d-spacing values are given in Appendix B (Table B.2). Figure 7.2 shows the x-rays diffraction patterns for samples 10% (w/w) metal doped cement.

Table 7.1: Qualitative x-ray results, in cps, of the main crystalline phases for OPC-doped cement

Sample	Environ.	Portlandite	C_3S	Calcite	Aragonite	Ettrigite	Gypsum	Calc./ Arag. ratio
1%Cd	N_2	149	267	127	-	61	25	8.6
	CO_2	64	237	328	38	28	29	
5%Cd	N_2	106	239	108	-	50	-	6.8
	CO_2	89	198	354	52	30	43	
10%Cd	N_2	248	470	132	-	55	-	5.7
	CO_2	106	113	401	70	41	29	
1%Pb	N_2	189	149	124	-	46	20	4.5
	CO_2	114	130	213	47	-	32	
5%Pb	N_2	180	195	153	-	48	-	3.9
	CO_2	79	126	242	62	24	22	
10%Pb	N_2	155	157	138	-	53	20	6.6
	CO_2	100	118	246	37	29	18	
1%Ni	N_2	109	109	136	-	46	25	4.2
	CO_2	73	95	357	84	-	29	
5%Ni	N_2	103	132	111	-	59	12	3.1
	CO_2	80	110	345	102	32	19	
10%Ni	N_2	131	129	121	24	61	33	3.1
	CO_2	-	95	378	123	-	47	
1%Zn	N_2	130	182	85	-	48	22	1.7
	CO_2	119	155	131	75	24	32	
5%Zn	N_2	256	689	188	-	68	-	1.5
	CO_2	133	189	178	115	24	19	
10%Zn	N_2	177	257	184	-	52	17	1.9
	CO_2	-	79	245	126	-	22	
Control	N_2	136	149	99	-	55	16	-
	CO_2	81	100	419	-	-	24	

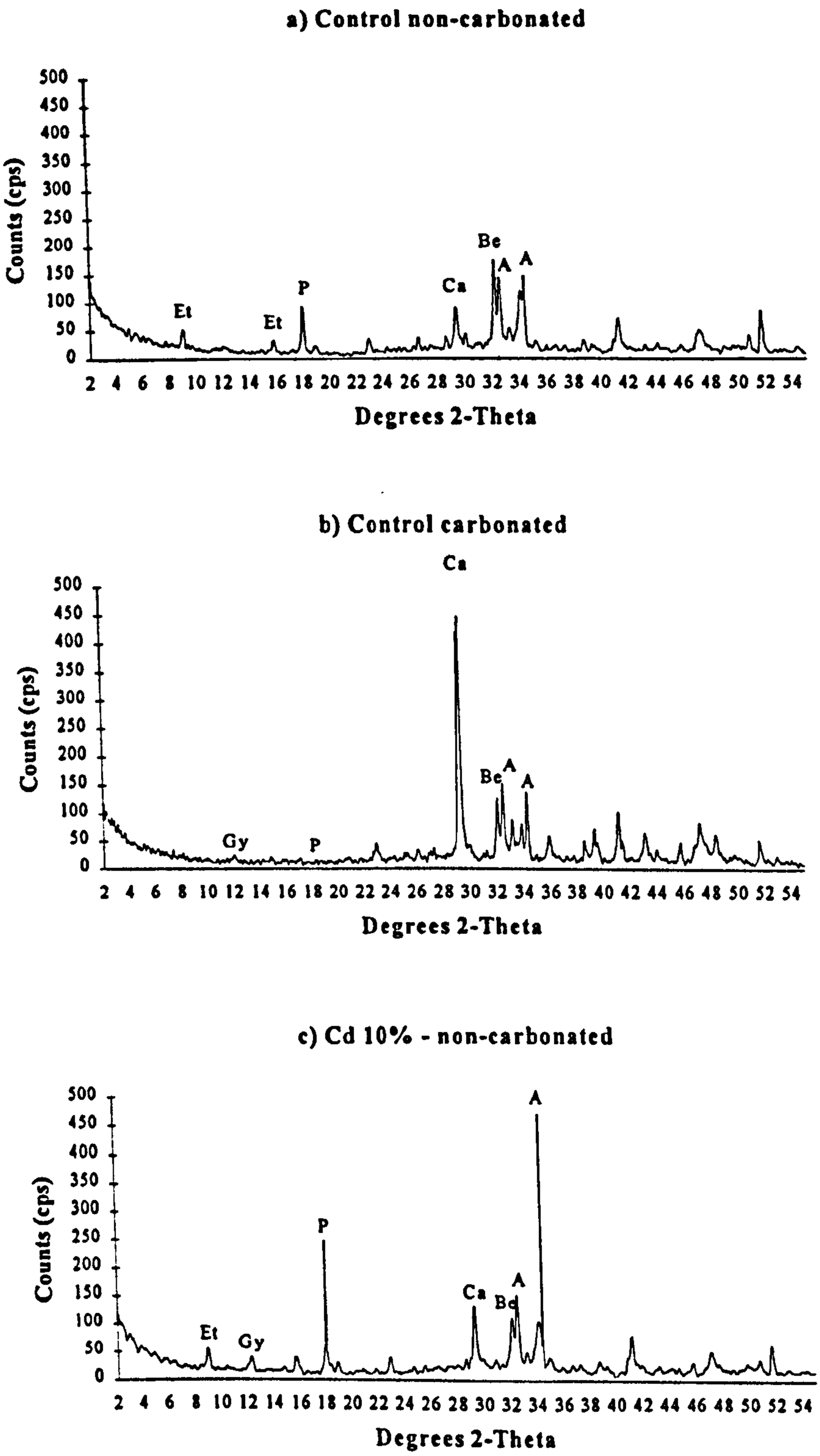
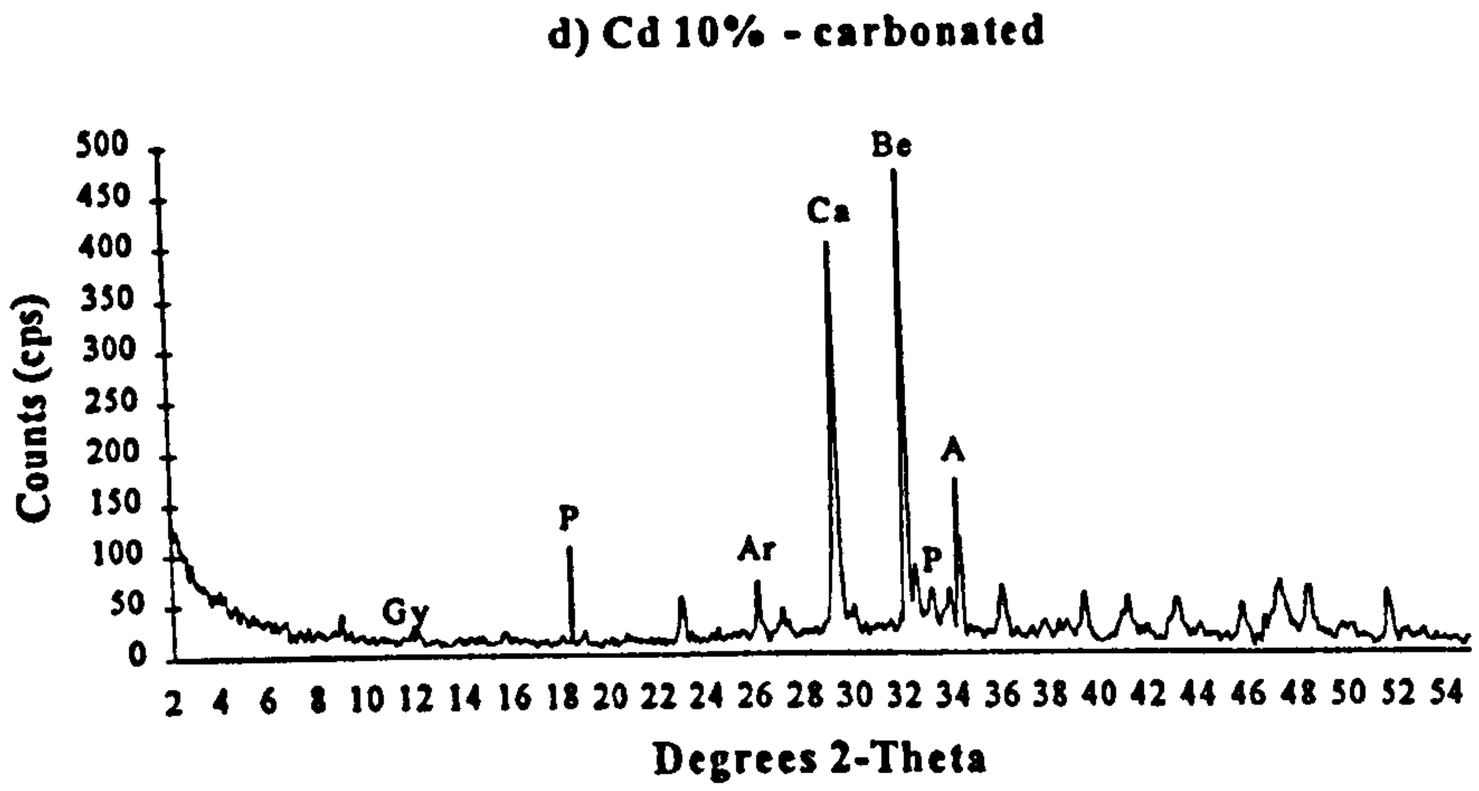
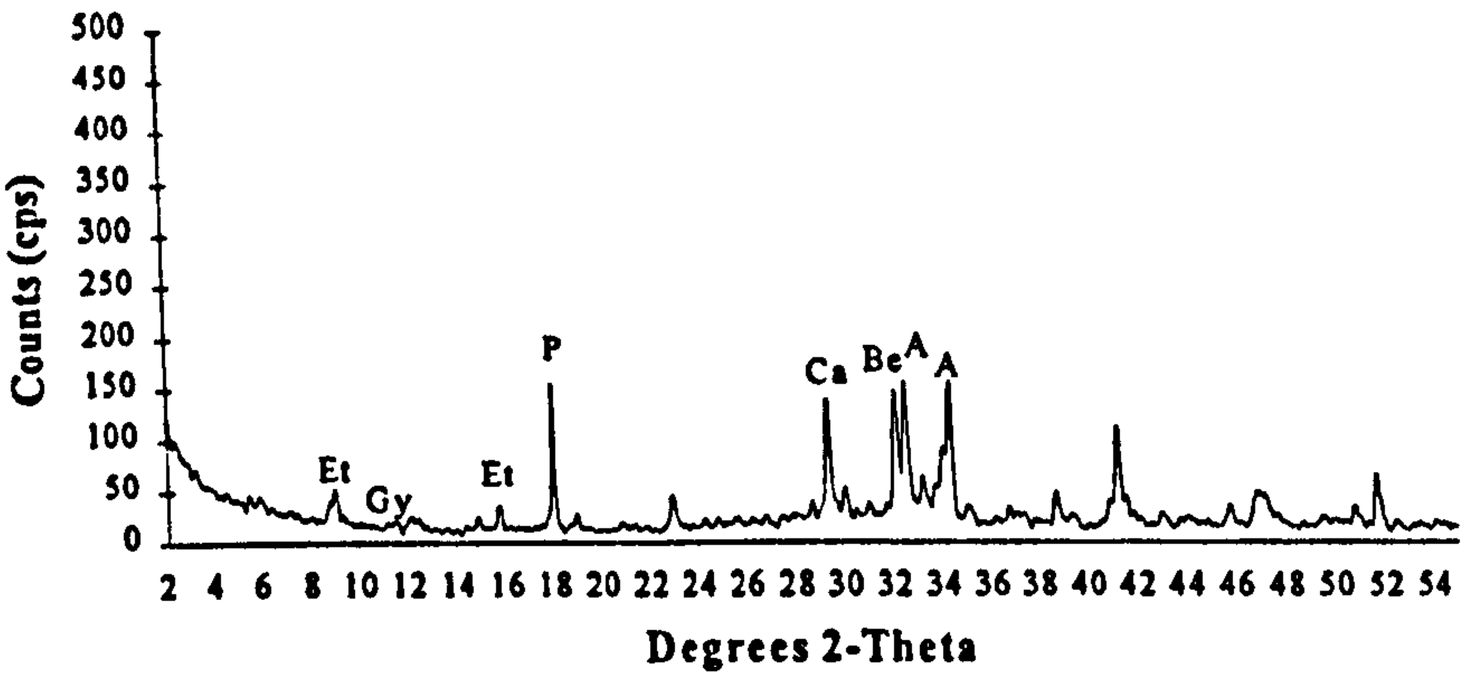
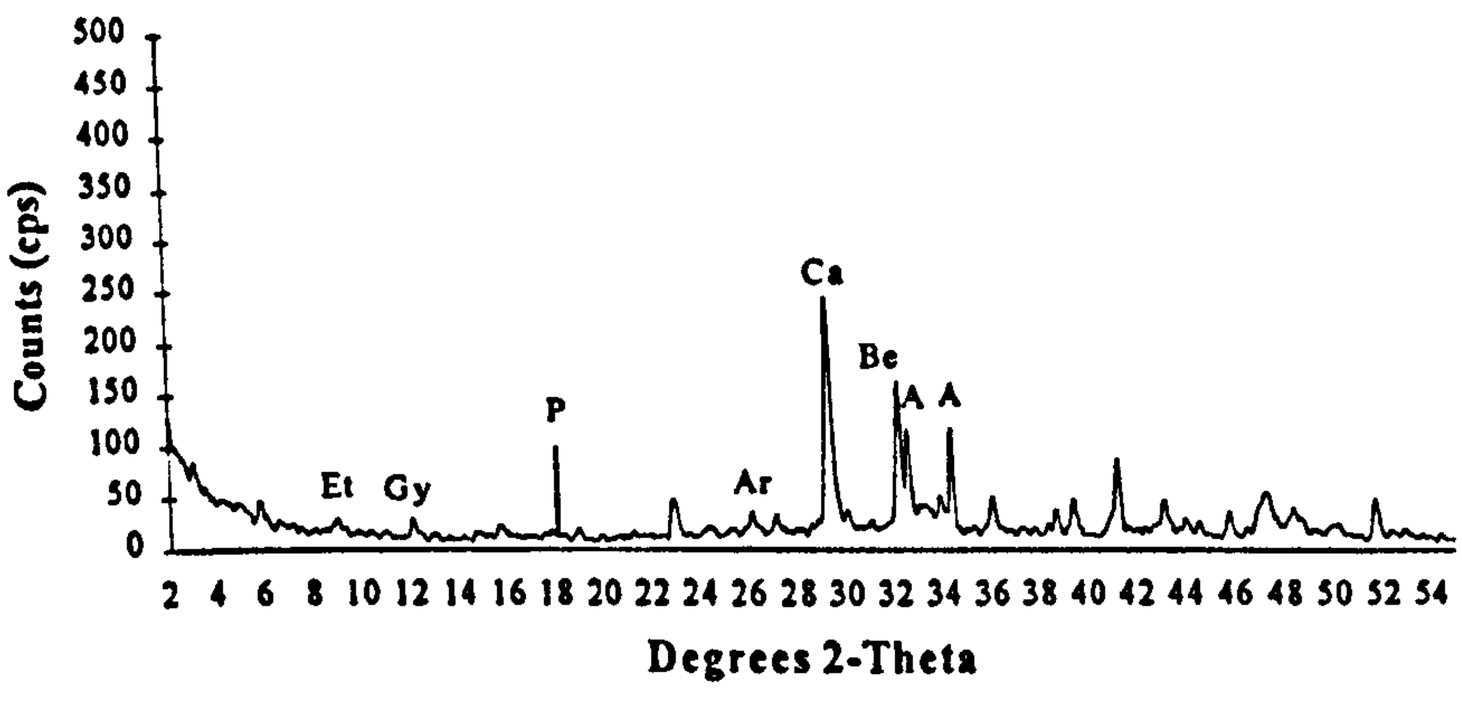


Figure 7.2: Qualitative x-ray diffractograms, where: Et= ettringite; Gy= gypsum; A= alite; Be= belite; P= portlandite; Ar= aragonite; Ca= calcite







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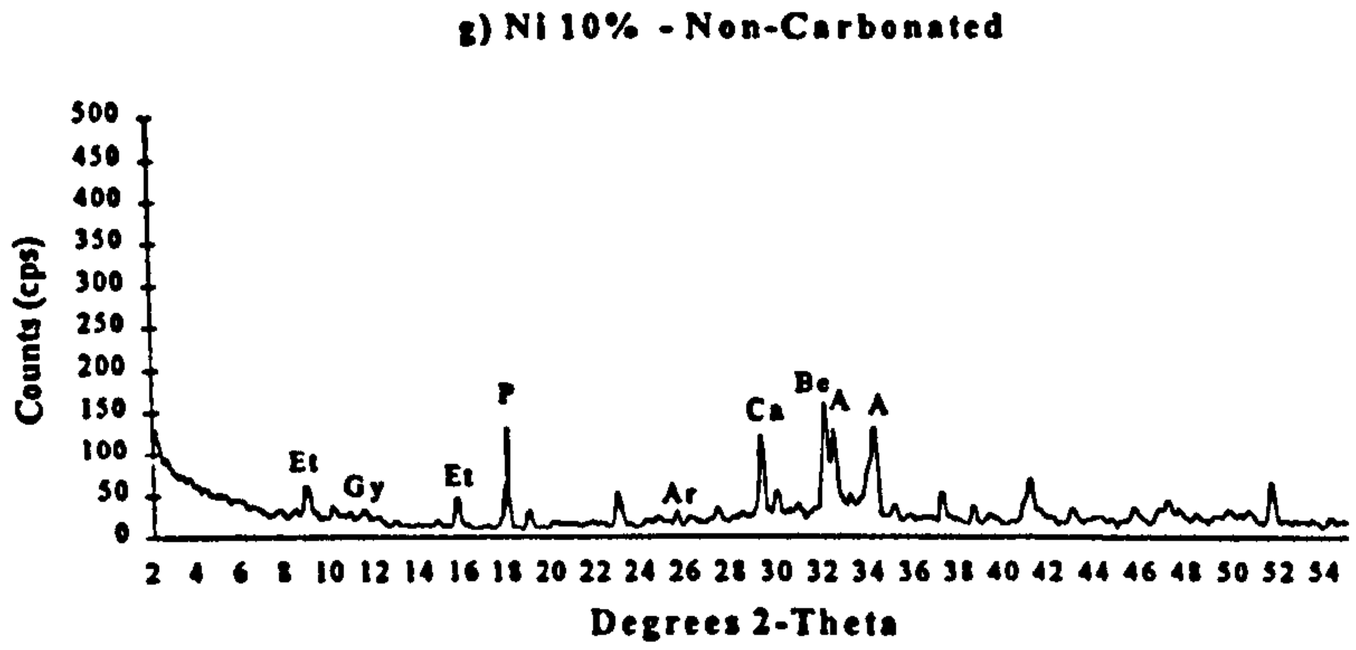


Figure 7.2: Qualitative x-ray diffractograms, where: Et= ettringite; Gy= gypsum; A= alite; Be= belite; P= portlandite; Ar= aragonite; Ca= calcite

The results obtained for the single metal doped cements were similar in mineralogy to the industrial waste specimens. Samples submitted to an accelerated carbonation program had an increase in the proportion of calcite, lower amounts of unhydrated alite and portlandite. Ettringite was not detected in most of the samples. However, three distinct observations could be made from OPC doped with single metal solutions. They were:

- Aragonite, a $CaCO_3$ polymorph, was present in all metal-samples, except the control.
- As the ratio calcite/aragonite approached 1.0, lower proportions of unhydrated alite and portlandite were present in the sample.
- By increasing the metal load, a slight increase in the % of $CaCO_3$ was observed and this is contrary to the trend noticed by Bonen et al. (1995).
- Regardless of the metal loading these results demonstrated that heavy metal doping increases the vulnerability of the paste to carbonation. Zn 5-10% and Ni 5-10% carbonated samples also showed the highest amounts of aragonite. However, it was noted that the carbonated Zn and Ni (10% w/w) samples were very friable in nature.

SEM Observations

The morphology of the carbonated doped-cement matrix differs significantly from that of specimens hydrated in nitrogen. As for the industrial waste samples, the reaction appears to involve both, inner and outer portions of the samples. For all four metals examined there were similarities, for example, Plates 7.1 and 7.2 show a non-carbonated sample of OPC doped with Zn (10%). These, showed some normal hydration phases, as ettringite, C-S-H and portlandite, though the material was very granular and weak in nature. Plates 7.3, 7.4 and 7.5 show the BEI micrographs of the carbonated analogue. In Plate 7.3 the typical surface of outer portion of the specimen is shown. Calcite needles were developed in abundance, throughout the sample. Plate 7.4 shows the interior portion of the sample, where euhedral and acicular calcite crystallites were abundant. Plate 7.5 shows these calcite crystals and C-S-H growing inside a void. The carbonated samples showed a more compact structure than their non-carbonated analogues.

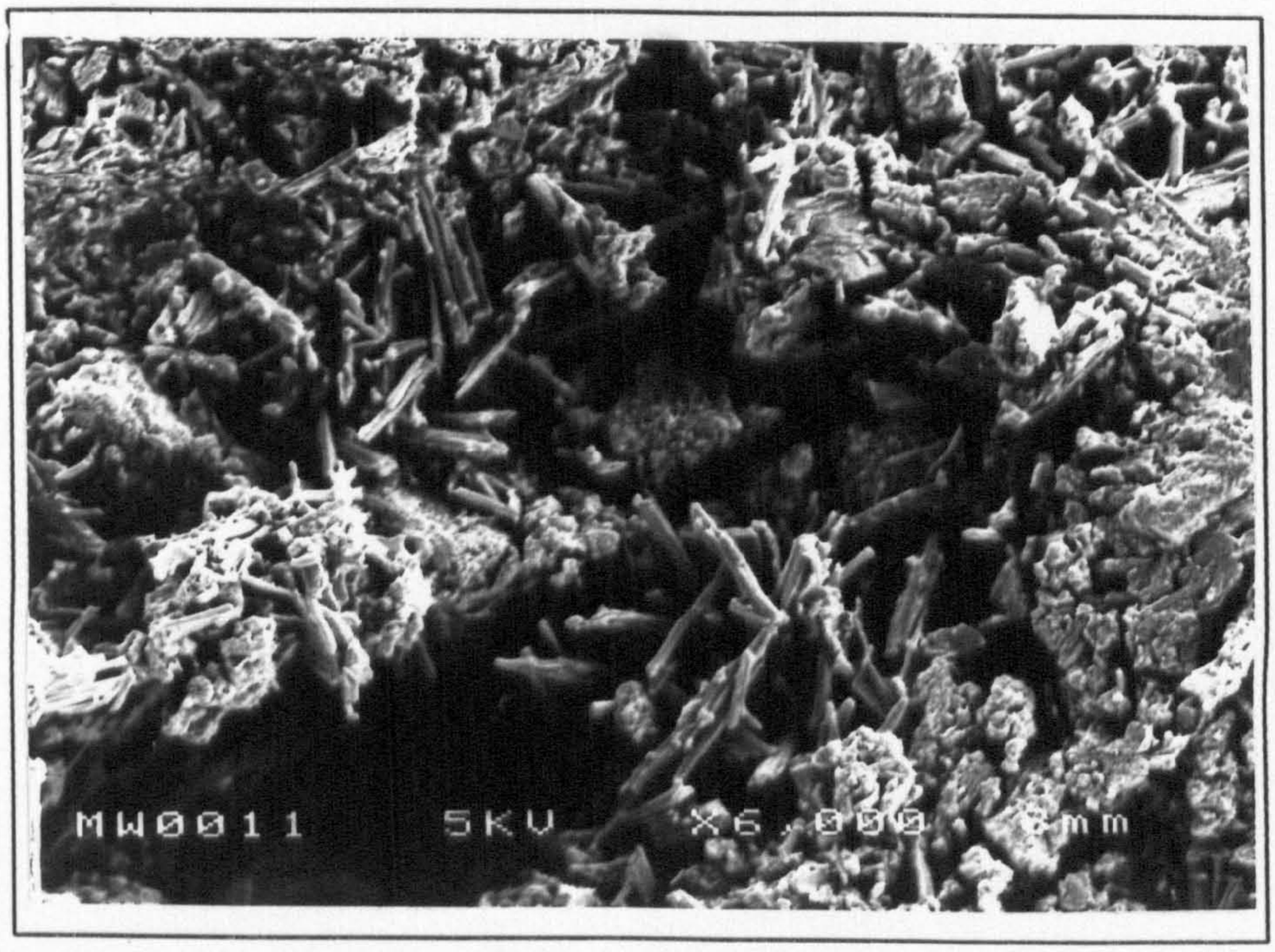


Plate 7.1: Fracture surface of the non-carbonated Zn-doped cement showing gel and ettringite

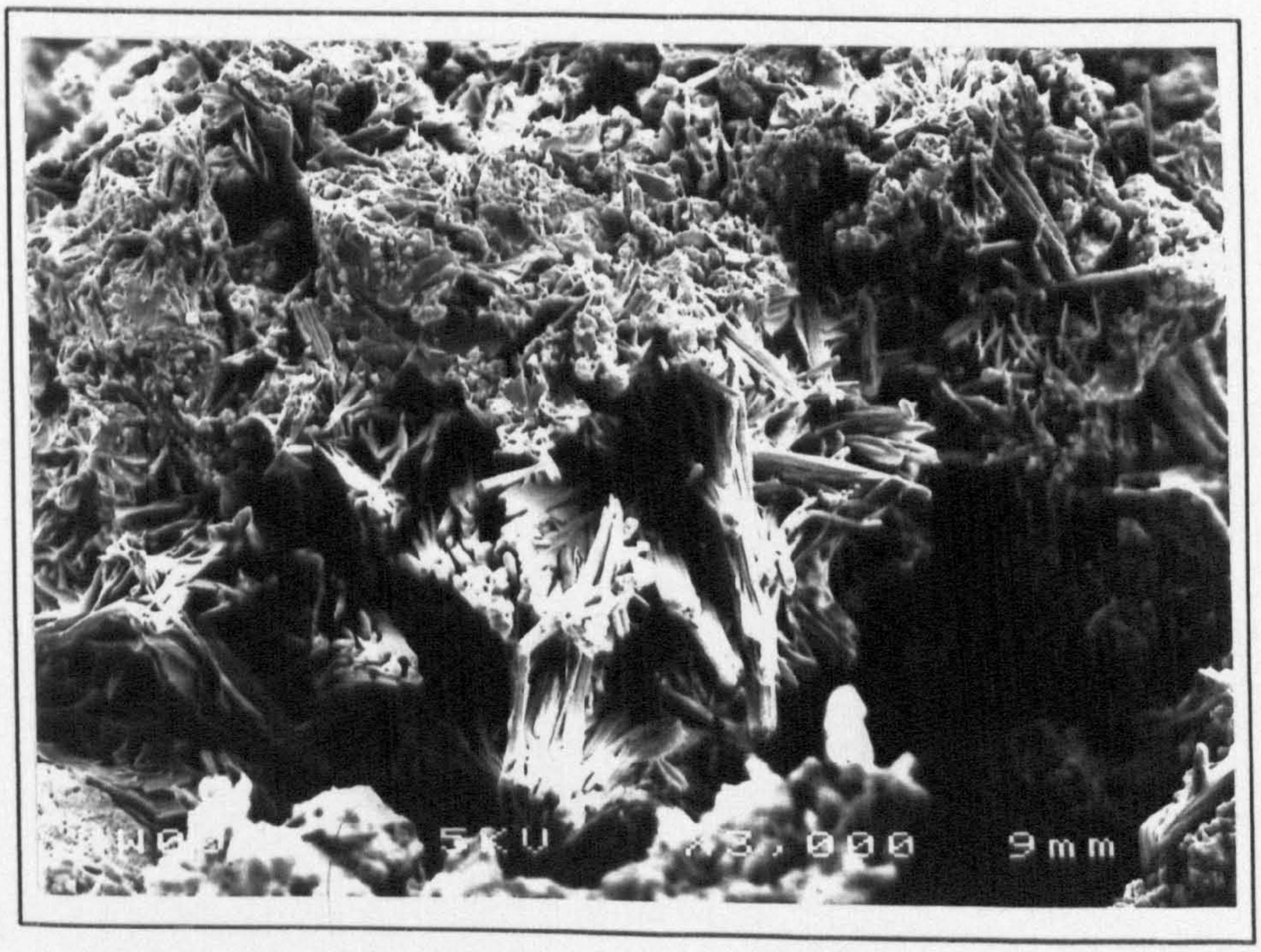


Plate 7.2: Fracture surface of a non-carbonated Zn-doped cement paste showing C-S-H gel and ettringite

Plate 7.3: Fracture surface of a carbonated Zn-doped cement paste showing the acicular calcite morphology

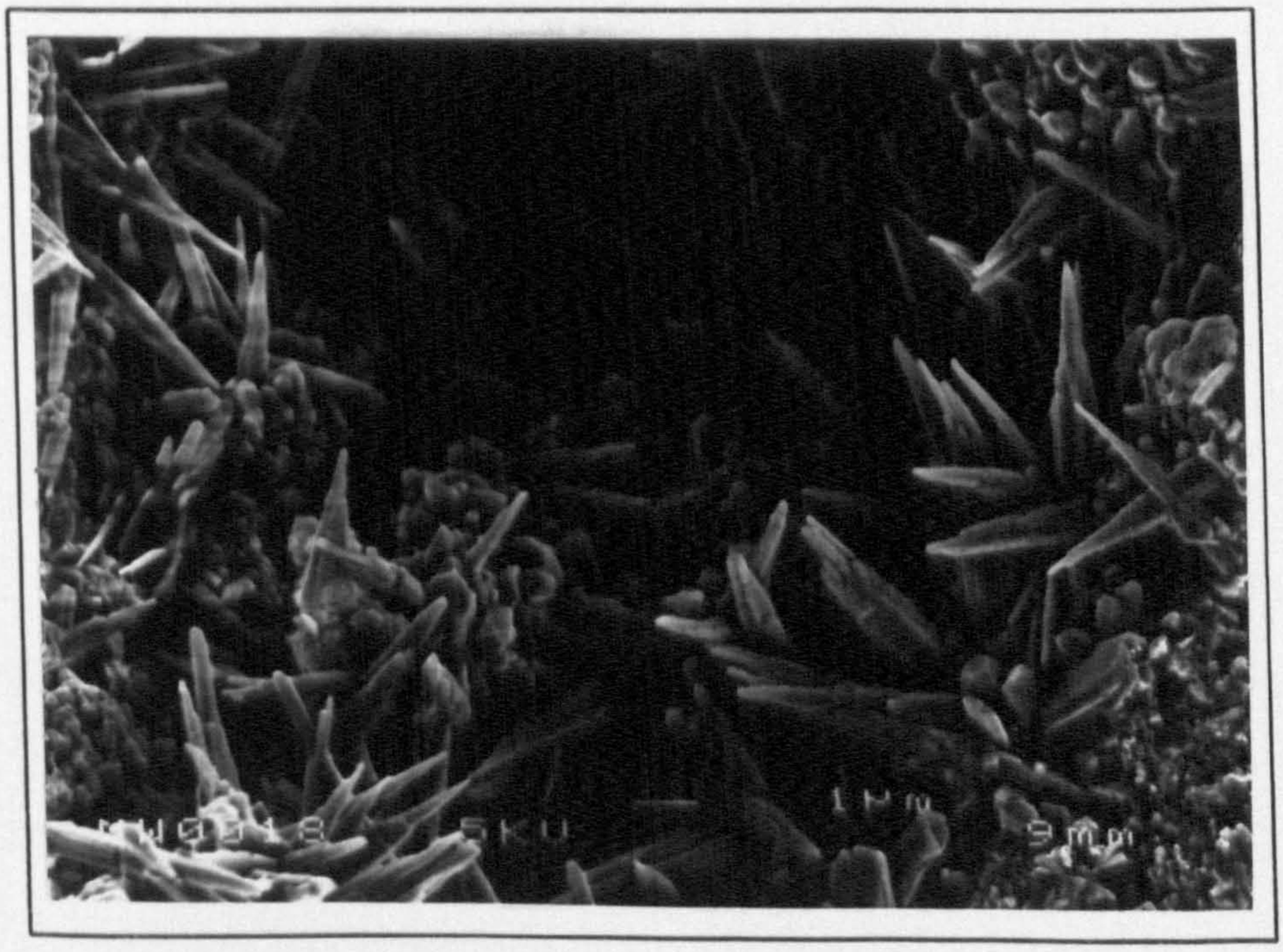


Plate7.4: Fracture surface interior of a carbonated Zn-doped cement paste showing both euhedral and acicular calcite crystals

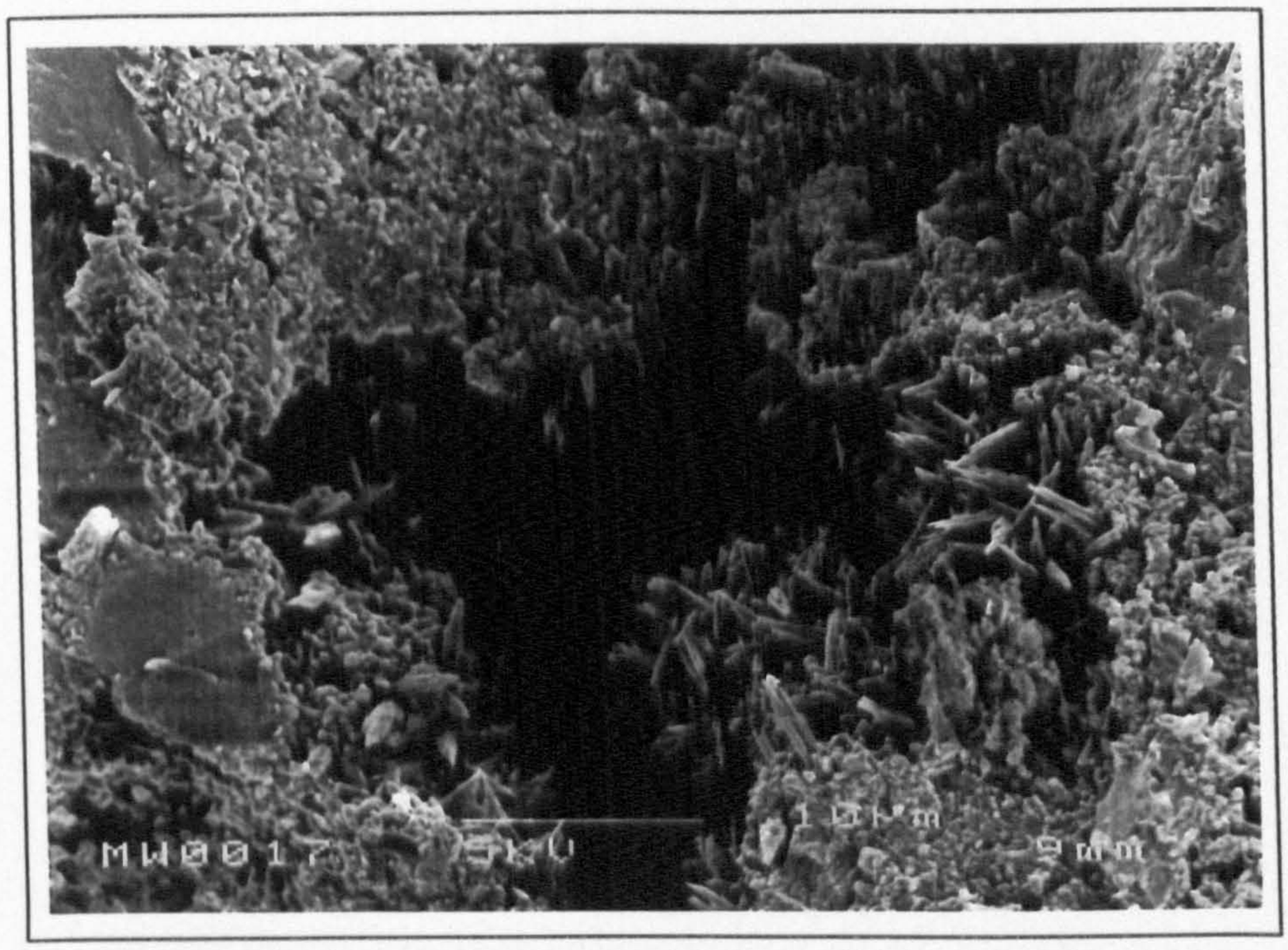


Plate 7.5: Fracture surface of a carbonated Zn-doped cement paste showing void filled with calcite crystals

DBI (digital backscatter imaging) micrographs of polished carbonated Zn-doped cement are shown in Plates 7.6 and 7.7. The mid grey tones of the matrix represent the modified C-S-H- matrix, rich in calcite precipitate whereas, white is anhydrous cement. The darker Si-rich rims, surrounding most of the C_3S grains, are noticeable as is the porosity that has developed (black).

EDAX analysis carried out on the 10% (w/w) doped samples are in Appendix D. The results are based on five measurements of each area analysed for each sample. They revealed a higher concentration of Zn and Pb inside the Si-rich rims while Cd and Ni were showed to be more dispersed in the C-S-H / calcium carbonate matrix and might indicate the existence of preferential sites for fixation for specific metals.

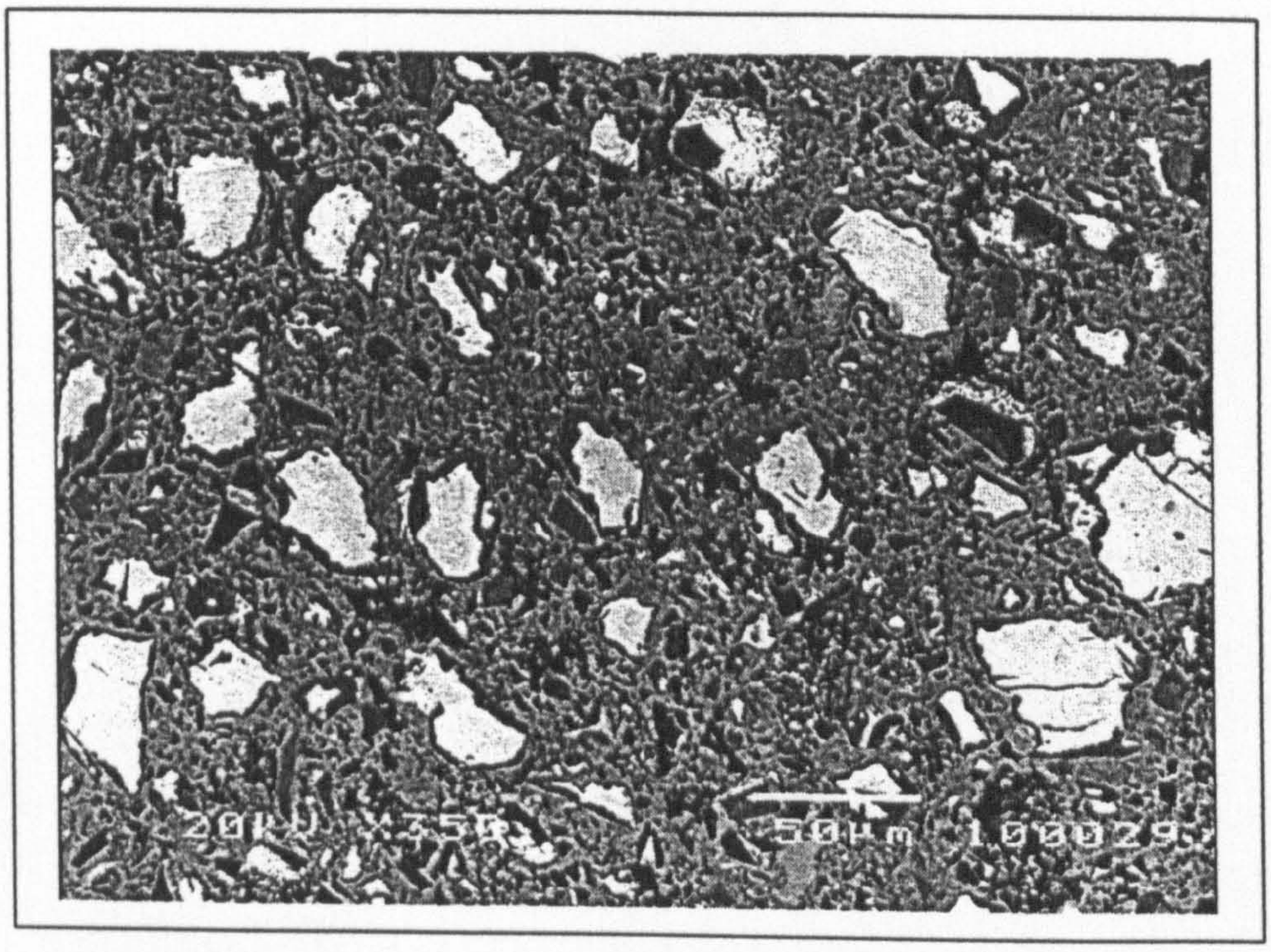


Plate 7.6: DBI micrograph of carbonated Zn-doped cement paste

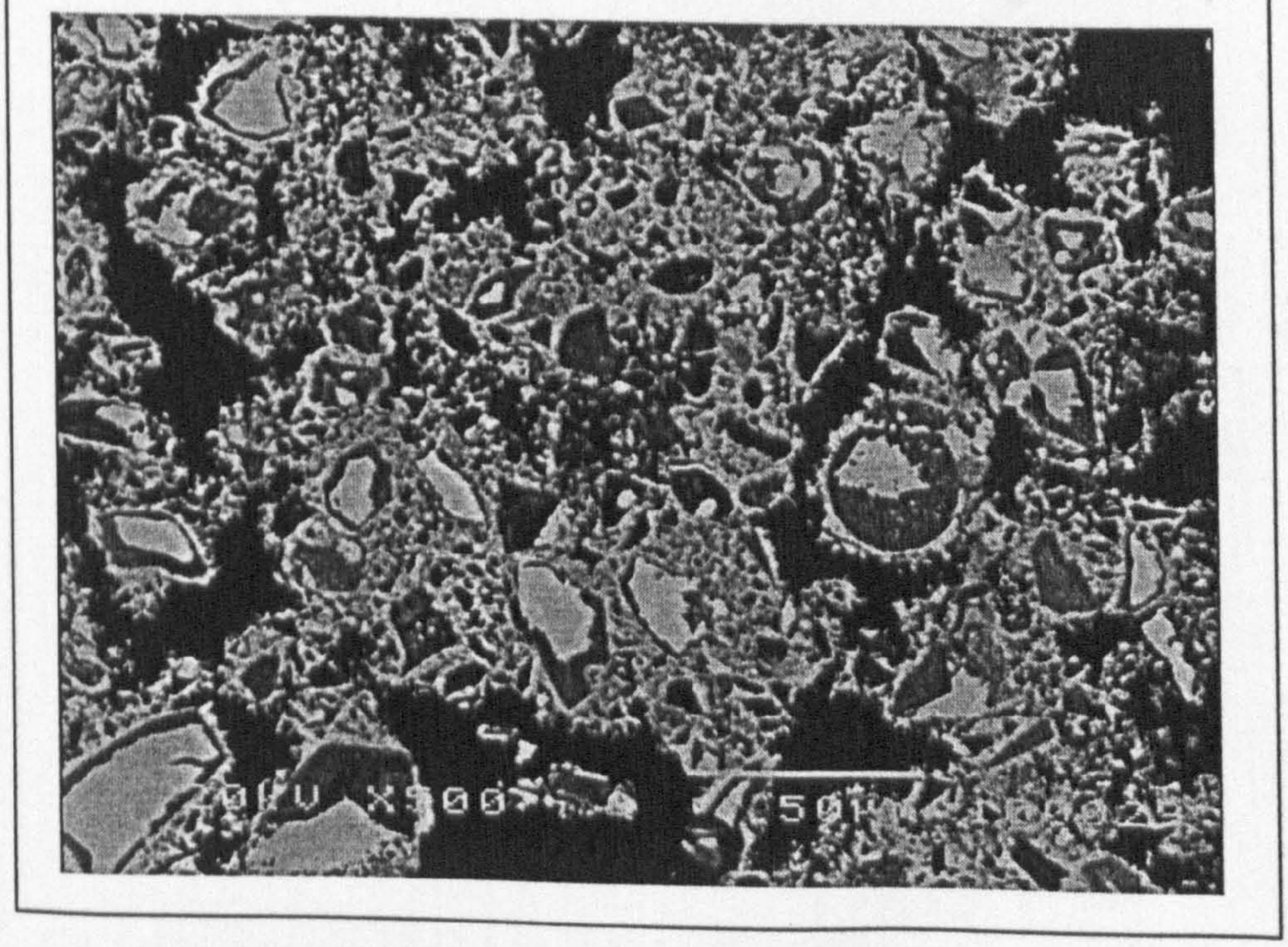


Plate 7.7: DBI micrograph of carbonated Zn-doped cement paste showing calcite crystals growing inside the pore space

FTIR Analysis

The FTIR results are summarised in Table 7.2 and their respective spectra are given in Figure 7.3. As no discernible effects were observed by FTIR spectra at lower concentrations this section shall consider only the results of the 10% (w/w) metal doped cement samples.

Table 7.2: Infrared spectral data for metal-doped cement systems,
where NC= non-carbonated and CA= carbonated

Mix	SiO_4^4 - (v3)	SiO_4^4 - (v4)	H_2O v1+v2	OH $Ca(OH)_2$	HOH (v2)	SO_4^{2-} (v3)	NO_3^-	CO_3^2 - (v3)	CO_3^2 - (v2)	SiOH
Zn - NC	970	520	3421	3646	1649	-	1336	1420	874	-
Zn - CA	1009	-	3414	-	1642	-	1258	1492	854	820
Cd- NC	966	510	3427	3646	1653	1113	1384	1418	879	-
Cd- CA	1008	-	3414	-	1792	1107	-	1429	856	822
Pb- NC	962	-	3460	3640	1650	1110	1390	1437	873	-
Pb- CA	1009	515	3440	-	1648	1120	-	1445	859	819
Ni- NC	978	512	3440	3670	1650	1119	1390	1440	872	-
Ni- CA	1008	-	3444	-	1646	1110	1350	1444	856	822

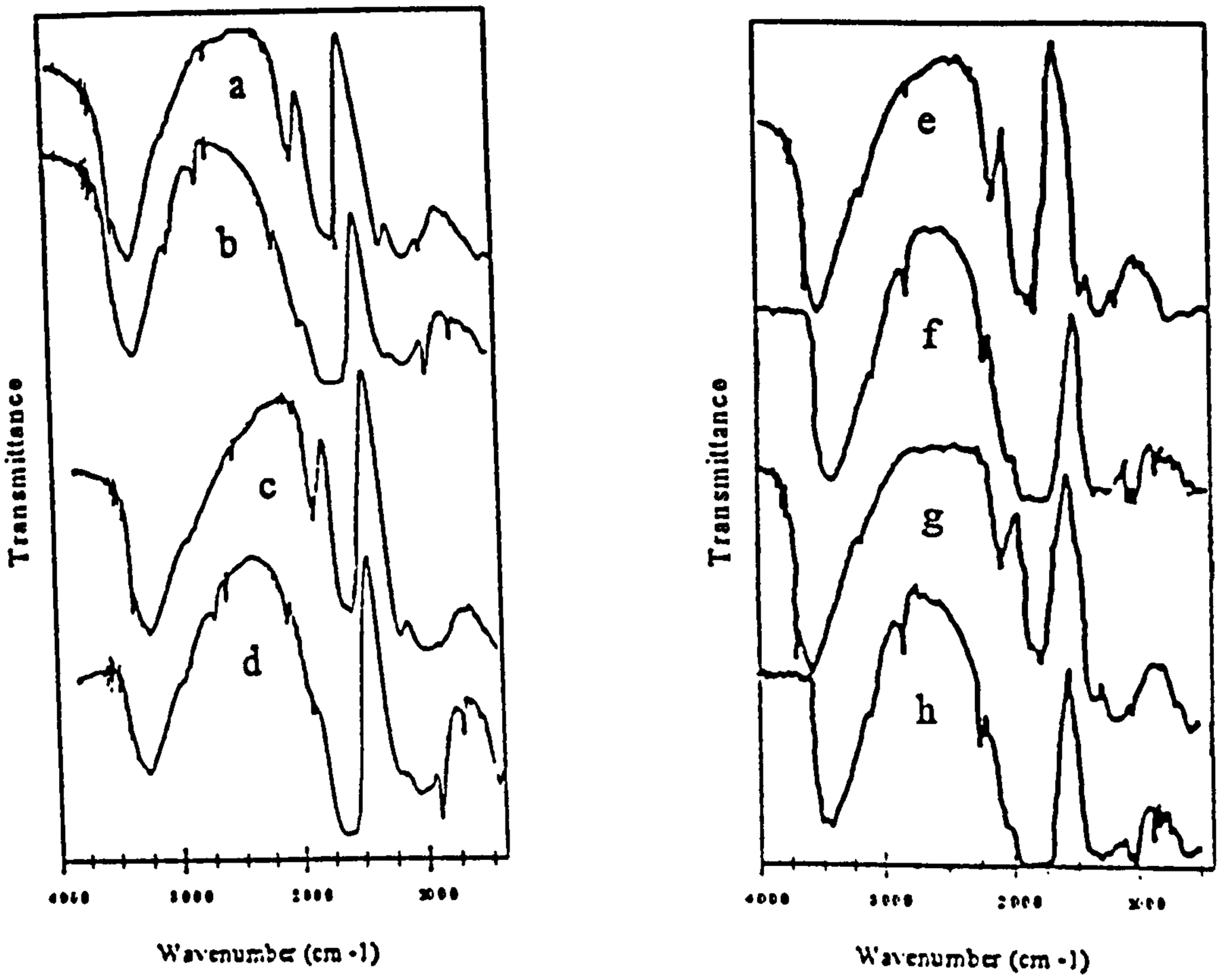


Figure 7.3: FTIR spectra - a) Cd-non-carbonated; b) carbonated; c) Pb-non-carbonated; d) carbonated; e) Ni-non-carbonated; f) carbonated; g) Zn-non-carbonated; h) carbonated

The systems doped with metals Cd, Pb, Ni and Zn, gave similar spectra. The main vibrational frequencies present have already been discussed in Chapter 5 for industrial waste/binder systems. The waveband at 1390 cm^{-1} is due to nitrate, and is overlapped with $\nu 3\ CO_3^{-2}$ for some of the carbonated samples. The OH-group band at 3640 cm^{-1} had a low intensity probably indicating a complete conversion of calcium hydroxide to calcite during carbonation. Ettringite (non-carbonated samples) and gypsum (carbonated samples) were identified in most of the samples. The $\nu 2\ CO_3^{-2}$ band was split for all carbonated specimens showing that both calcite and aragonite were present. The band for alumina-gel (weak band) was detected for samples doped with Pb and Ni only. This could indicate that the decomposition of ettringite by carbon dioxide to an aluminate phase has occurred. This phase, if deprotonated, migth bound with dissolved metal ions, such as Pb or Ni (Kinniburgh et al., 1981).

7.4.2 Leaching Characteristics

Table 7.3 presents the analytical results of the leaching test extraction of the doped-cement at different metal concentration. The pH values for the carbonated samples after 24 hours were between 7.5 and 8.5.

The results show that carbonated samples gave a better leaching performance in comparison to non-carbonated analogues, up to 5% dose. At 10% the results were similar, except for Cd.

Table 7.3: Leachate metal concentration (mg/L)

Samples	Environment	Metal Concentration	ESD*
1% Cd	N_2	0.19	± 0.01
	CO_2	0.05	± 0.02
5% Cd	N_2	2.98	± 0.40
	CO_2	0.09	± 0.01
10% Cd	N_2	4.02	± 0.38
	CO_2	0.31	± 0.04
1% Pb	N_2	1.05	± 0.06
	CO_2	0.03	± 0.02
5% Pb	N_2	2.84	± 0.26
	CO_2	0.99	± 0.41
10% Pb	N_2	6.12	± 0.06
	CO_2	5.39	± 0.36
1% Ni	N_2	1.34	± 0.17
	CO_2	0.07	± 0.03
5% Ni	N_2	3.59	± 0.09
	CO_2	1.80	± 0.21
10% Ni	N_2	7.20	± 0.29
	CO_2	6.87	± 0.12
1% Zn	N_2	0.31	± 0.02
	CO_2	0.10	± 0.03
5% Zn	N_2	1.98	± 0.09
	CO_2	0.83	± 0.10
10% Zn	N_2	2.41	± 0.11
	CO_2	2.99	± 0.01
Control	N_2	<0.01	-
	CO_2	<0.01	-

Note: ESD* = estimated standard deviation (mg/L)

7.5 DISCUSSION

The results showed that improved physico-chemical properties for all samples submitted to the accelerated carbonation program could be realised. The chemistry is complex and

the carbonation reaction very severe, however, the interaction between the cement paste and metal waste species indicates the following mechanisms by which these metals are immobilised:

- They can precipitate with the anions, released during hydration of the clinker (silicates);
- They can become part of the decalcified C-S-H/calcite matrix, by either being precipitated as carbonated specie or being adsorb by the decalcified silica gel;
- They can adsorb onto the ionic surface of the cement grain, however for highly carbonated specimens this chemisorption will precede precipitation forming solid solutions;

These mechanisms will be discussed further below.

Examination by X-RD gave similar results to the industrial waste samples previously studied (section 6.3.2). The findings suggested that cement hydration was accelerated, despite the presence of retarders such as Zn and Pb. By requiring more ions Ca^{+2} to be dissolved on reaction with CO_2 to form solid $CaCO_3$ cement hydration is initiated. The process starts when Ca^{+2} was provided by any $Ca(OH)_2$ and C-S-H present, forming $CaCO_3$ (nucleation + precipitation). Portlandite was dissolute in Ca^{+2} and OH^- and C-S-H was decalcified into a silica-rich pseudomorphic structure, converting ultimately to a silica-gel, into which $CaCO_3$ was firmly precipitated as aragonite and calcite. Ni and Zn (10%) doped samples were associated with higher amounts of aragonite. The presence of aragonite (the metastable polymorph of calcite) could be explained by the variation of humidity and temperature that occurs during the carbonation reaction.

The presence of metals also increased the susceptibility of cement paste to carbonation. This observation combined with an acceleration of the hydration reaction suggested that a change in pore size distribution and hence, permeability was occurring and, that metal cations were either precipitated as carbonated salt or being bound with Si-rich structures. Diffractograms of the Pb and Cd doped samples showed numerous peaks that could be associated with cerrusite ($PbCO_3$) and otavite ($CdCO_3$).

Electron probe microanalysis of the metals indicated selectivity in the location of Cd and Ni in the decalcified C-S-H/calcite matrix, whilst Zn and Pb were found in Si-rich rims around the clinker grains and in the matrix. The fact that Ni^{+2} could replace Ca^{+2} in the C-S-H phase was shown previously by Komarneni et al. (1986), and in the present study both, Ni and Cd, evidence suggests precipitation as their respective carbonate. The ion K^{+} was noticeable redistributed into the rich Si-rim when samples were carbonated. Cocke at al. (1990) and McWhinney et al. (1990a, 1990b and 1993) have reported a re-location of potassium in the surface of the cement paste for many metal-doped cements. In carbonated samples, K^{+} may act as a charge compensation cation, suggesting that metals were deposited in the solid state living the NO_3^{-} anion "free".

The infrared analysis showed definite structural change in the silicate spectra of carbonated samples. An exposure to an accelerated carbonation regime, samples presented the $\nu 3$ band of SiO_4^{-4} at a higher energy and reduced intensity compared to the nitrogen cured one. These vibrational changes are indicative of increased polymerisation of silica units. Silanol peaks were also identified in the spectra of carbonated samples and it may be that another mechanism of fixation, silicate precipitation, may be in operation here.

Silicate reactions with metals have been discussed widely by Vail (1952), Iler (1979), Petit et al., (1980), Falcone (1982) and Bishop (1988). These reaction products are usually non-crystalline and therefore very difficult to characterise structurally. They are most often described as hydrated metal ions associated with silica or silica gel (Conner, 1990).

Important information was obtained by FTIR in the spectra between 3650-3400 cm^{-1}. Metal salts, such as $Pb(OH)_2$ or $CaZn_2(OH)_6.2H_2O$ are shown at these frequencies as sharp bands, such as given by the nitrogen cured samples. However, in carbonated samples the peaks were broader indicating that the formation of these salts did not take place or they have reacted with CO_2.

Aliguie et al. (1982) and Cocke et al. (1990) have established that the rate-retarding effect of lead and zinc have been proposed to be due to the coating effect of

$CaZn_2(OH)_6.2H_2O$ and different lead salts around the clinker grains, avoiding the contact of the C_3S with water.

The results obtained here have demonstrated that these retardation effects may have been overcome during carbonation, by the removal of calcium ions, as already discussed, to form carbonates, thus accelerating the hydration of reaction clinker, and by the reaction of the metal salts themselves with carbon dioxide to form calcium and their respective metal carbonates. The reaction, below, is an example of the reaction of $CaZn_2(OH)_6.2H_2O$ and CO_2.

$$CaZn_2(OH)_6.2H_2O + CO_2 \rightarrow CaCO_3 + 2ZnCO_3 + 5H_2O \qquad \text{(Eq. 7.2)}$$

The broad and strong bands exhibited at 1445-1420 cm^{-1} are due to CO_3^{-2} and therefore may be attributed to $CaCO_3$, $ZnCO_3$, $PbCO_3$, $NiCO_3$ and $CdCO_3$ salts.

Leachate analysis gave significantly lower extraction results for carbonated specimens. However, samples with a metal load over 5% showed that the effects of using carbonation was less apparent suggesting that metal fixation is limited by the amount of metal present, which above certain limits could provoke a disequilibrium on the precipitation reactions, i.e., the chemical interactions may enhance the development of a complex relationship between porosity and permeability, allowing metals to leach out more easily.

The chemistry of carbonated waste forms is complex and different mechanisms for metal fixation are operating. First, the degree of hydration of the cement, which is accelerated by carbonation, and the influence of the dopant are of primary importance and the presence and the nature of water are critical. Second, the polymerisation of silicates, precipitation of the cations as silicates, carbonates and other salts have broad implications for solidification systems.

7.6 SUMMARY AND CONCLUSIONS

This part of the work confirms earlier results that carbon dioxide has significant effects on the hydration of cement in a metal-doped paste. XRD results indicate abundance of $CaCO_3$ for the carbonated specimens, with a reduced amount of C_3S and portlandite. $CaCO_3$ is present in two forms, i.e., as calcite and as aragonite. Metals dopants such as Zn and Ni gave higher amounts of aragonite. Metal-doped cement was more vulnerable to carbonation, as shown by the increase in the amount of calcite as metal loading increases.

Two defined zones were found within and around the clinker grains as a result of carbonation: a Si-rich rim and a decalcified C-S-H / calcite matrix. Microprobe analysis showed that the metal location can be selective. Cd and Ni were preferentially located in the decalcified gel/calcite area, while Zn and Pb were found in both.

Analysis by FTIR showed that metal bond and hydrogen bonded hydroxide bands disappeared due to accelerated carbonation. An increased degree of polymerisation of the silicate hydrates was also observed and metals are suggested to be precipitated as silicates, as silanol groups were also identified.

The leaching results indicated that improved metal fixation for carbonated samples up to 5% metal doped system was easily obtained. Metals were stabilised in their respective carbonate salts, which have a lower solubility at pH 7.5-8.5 (lechate pH).

These conclusions show that important changes are caused by carbonation to both the physical and chemical properties of waste forms by the formation of different solid assemblage, which cause precipitation in the pores and consequent change in permeability, sorptive potential and pore water chemistry.

CHAPTER 8

GENERAL DISCUSSION

8.1 GENERAL

The work presented in this Thesis investigates the effects of natural and accelerated carbonation on the development of mechanical and microstructural properties of solidified products. Carbonation was found to produce physical and chemical changes in the microstructure of the cement-based materials, resulting in increased metal binding capacity.

These findings are important for cement-based solidification technology, mainly because of the need for new processes and systems to treat hazardous wastes prior to landfill. In previous observations, carbonation was found to be a common phenomenon for cementitious materials as well as for solidified wastes left in contact with air. However, it was normally associated with deleterious effects, e.g. a drop in pH of the pore solution causing corrosion of steel reinforcement, and where solidification is concerned, increased solubility of some metals , etc.

In this study the effects of carbonation upon solidified waste forms have been shown to be beneficial. The reported effects of poisoning or retardation of the hydration reactions of the cement by the presence of waste appeared to be partially overcome. Strength development was greatly enhanced; and microstructural characteristics were affected primarily by the precipitation of calcite in the pore structure and as part of the cementitoius matrix itself, suggesting that metals were bound to the matrix either by adsorption or precipitation as complex carbonated species. Polymerisation of silicates has also occurred, and might take a part in the process of fixation of metals.

Two industrial wastes, a plating waste and a commercially blended waste, were examined in detail, and they were shown to behave differently in the presence of carbon dioxide, indicating the importance of waste composition. Also, the use of different hydraulic binders were shown to cause distinct effects upon the carbonated waste forms.

Furthermore, the kinetics of the carbonation reaction for the different waste/binder systems showed that the degree of carbonation varied according to mix design and waste addition, whether complex or simple.

These results have shown the potential importance of a controlled carbonation reaction to obtain enhanced chemical and physical qualities in solidified waste forms. However, any assessment of the carbonated solidified product should consider long-term effects to ensure optimum disposal properties.

8.2 CEMENT-BASED SOLIDIFICATION

Solidification processes have been used to manage numerous types of wastes worldwide, however, the fundamental chemistry and microstructure of these waste forms is not well known, although many workers have commented on the importance of the solidifying reactions (Clements et al., 1985; Conner, 1990; Cocke, 1991).

Nevertheless, many difficulties have been associated with wastes that have failed to solidify in the past, and these have resulted in well founded fears in the community regarding environmental damages (ENDS, 1992). Rising standards in Europe, with tightening EC legislation (Landfill Directive and Landfill Tax Regulation) may restrict the types of waste acceptable at landfills, and consequently encourage many industries to submit their waste to more effective treatment before landfilling. Therefore, there is an urgency for the effective development of new processes/research in solidification technology, to successfully conditioning the waste, to enable release limits to be achieved.

An appreciation of the advantages of cement-based solidification can be obtained by considering the vast quantity of binder matrices, and the versatility of these matrices to encapsulate dusts, liquids and sludges, greatly reducing the dispersion on the environment. Moreover, the use of cements is of publicaly acceptable and economically sound.

Workers such as Bhatty (1986), Bishop (1988), Conner (1990), McWhinney et al. (1990) have investigated the hydration reactions of the most common solidification

binder, OPC, when in contact with waste materials. Basically, they found that, despite some specific interference effects Portland cement hydrates to a dense interlocking network of hydration products that physically encapsulate waste materials while the release of calcium hydroxide, as portlandite, maintains high pH conditions ensuring the insolubility and hence fixation of metallic species.

The reviews carried out by these and other workers linked the waste/binder interference effects to specific compounds such as zinc and cadmium. However, the research cited had been carried out in the laboratory, using reagent grade materials. Nevertheless, these results are fundamental and provide most of our current knowledge in this field.

In the 1990's work involving real waste was published (Claudio, 1991; Hills, 1993 and Hanna et al., 1995). These works gave new insights into the importance of waste characteristics on retarding, inhibiting and accelerating waste/cement reactions. These effects are many and varied and are not simple to predict from knowledge of the composition of the waste and may be responsible for retardation/acceleration or "poisoning" effects (Poon et al., 1985; Cartledge et al., 1990; Hills et al., 1992; Roy et al., 1992; Akhter et al., 1993; Hills et al., 1994 and Trussell et al., 1994). The general effects are complicated as factors such as pH, redox potential, metal speciation, chemical reactions (precipitation, adsorption, etc.) are of most importance to solidification.

One chemical reaction that is known to influence solidification of waste forms is carbonation, however, up to now very little attention has been giving regarding its application to solidification technology (Mollah et al., 1993).

In this research programme the application of carbonation during solidification of real wastes and laboratory grade materials has revealed many new features of the cement/waste hydration reactions, and also important physico-chemical changes in the solidified product. Examination of the carbonated solidified wastes showed them to be rich in calcite precipitates in a highly polymerised silica gel. They also exhibited enhanced strength development and improved metal fixation characteristics. The mechanisms by which carbonation aids encapsulation of metal species were

demonstrated to be complex and metal selective, and strictly dependent on water content and binder type.

8.3 PHYSICO-CHEMICAL PROPERTIES OF CARBONATED SOLIDIFIED WASTE FORMS

The carbonation reaction was influenced by waste composition, cement type and moisture content. The two industrial wastes investigated behaved differently when exposed to carbon dioxide, showing that concentration of different species and metal speciation are fundamental. The presence of metals in cement paste general increased its susceptibility to be carbonated, and it is found that carbonation could overcome the effects of retardation of C_3S hydration (coating effect suggested by Aliguie et al., 1982; Cocke et al., 1990) by encouraging Ca^{+2} ions to react with CO_3^{-2} ions to form complex metal carbonates. Water content is also fundamental, and excess of water could slow down the reaction while no water at all could stop it. These parameters showed to be decisive keys to determine the kinetics of carbonation reaction. This work also shows that the total uptake of CO_2 was related to the improved mechanical and microstructural properties so thoroughly discussed, which are summarised below.

8.3.1 Strength Development

In the present study, one significant effect of carbonation upon waste forms was on strength, and this may due to an increase in the hydration of C_3S driven by the formation of calcium carbonate. Samples left in an accelerated carbonation regime reached strengths of several MPa after few minutes. This behaviour was investigated for cement mortars by Young et al. (1974). The precipitation of calcite also had a direct effect on filling porosity and precipitation of different waste species.

8.3.2 Microstructural Characterisation

During carbonation we have seen that the silicate phases were polymerised, that portlandite was converted to calcite and that aluminate phases, initially hydrated, were converted back to their tetrahedral forms, forming a mixed AlO_4/SiO_4 three dimensional network.

Backscattered imaging was used to characterise microstructure and showed that cement grains (C_3S) were surrounded by Si-rich rims, which were enveloped in a calcium carbonate/partially decalcified C-S-H matrix. The calcite crystallites were irregular and appeared to co-exist with the C-S-H. These structures contained significant quantities of impurities coming from the waste. AFt phases were not evident on the carbonated samples, suggesting their decomposition to calcite, alumina-gel and gypsum.

Metal species were noted to be present in two specific locations in the microstructure: a) calcite/partially decalcified C-S-H matrix; b) silica-rich rims. For some samples it was clear that these sites contained specific metals, i.e., were selective. For example, while Cd seemed to be preferentially located in the calcite/decalcified C-S-H matrix, Zn appeared at both. These findings are of particular importance and indicate the possible mechanisms of fixation in action. Four major factors or mechanisms are deduced to be responsible for metal fixation due to carbonation, and they are:

- Fixation involving the calcite/aragonite phases, which may happen through precipitation of the metals as carbonate salts. Also, because of the complex chemical composition of those systems, the probability of forming solid solutions is very high (Kinniburgh et al., 1981).

- The precipitation of carbonate species under favourable pH conditions can result in isomorphic substitution of metal atoms within the crystal structure, adsorption and entrapment by occlusion or in pore spaces. In certain cases, metal carbonates are less soluble than their corresponding hydroxides.

- The phenomenon of adsorption and formation of solid solutions act simultaneously. If a metal species cannot be incorporated readily into a crystal by precipitation it can be strongly adsorbed onto the surface to form a monolayer, which can slow crystal growth or/and change pattern of growth (e.g. the rhombic and acicular crystals in calcite). However, if the metal 'fits' into the crystal structure, it may contribute to crystal growth by forming a solid solution, or a nucleation site for further precipitation. It is important to note that adsorption is directly related to surface area, and consequently particle size (ion size) and porosity.

- A further fixation mechanism was based on the observation of a highly polymerised silicate structure and the presence of silanol groups. The reactions of polyvalent metal salts in solution with soluble silicates have been studied extensively over many years (Vail, 1952; Iler, 1979; Conner, 1990). Therefore, the presence of metals on the rich Si-rim surrounding the C_3S particle were associated to their coordination to silicates or silica gel, possibly to create metal silicates.

All these possible mechanisms, associated with carbonation, are illustrated with reference to a proposed simple model in section 8.4.

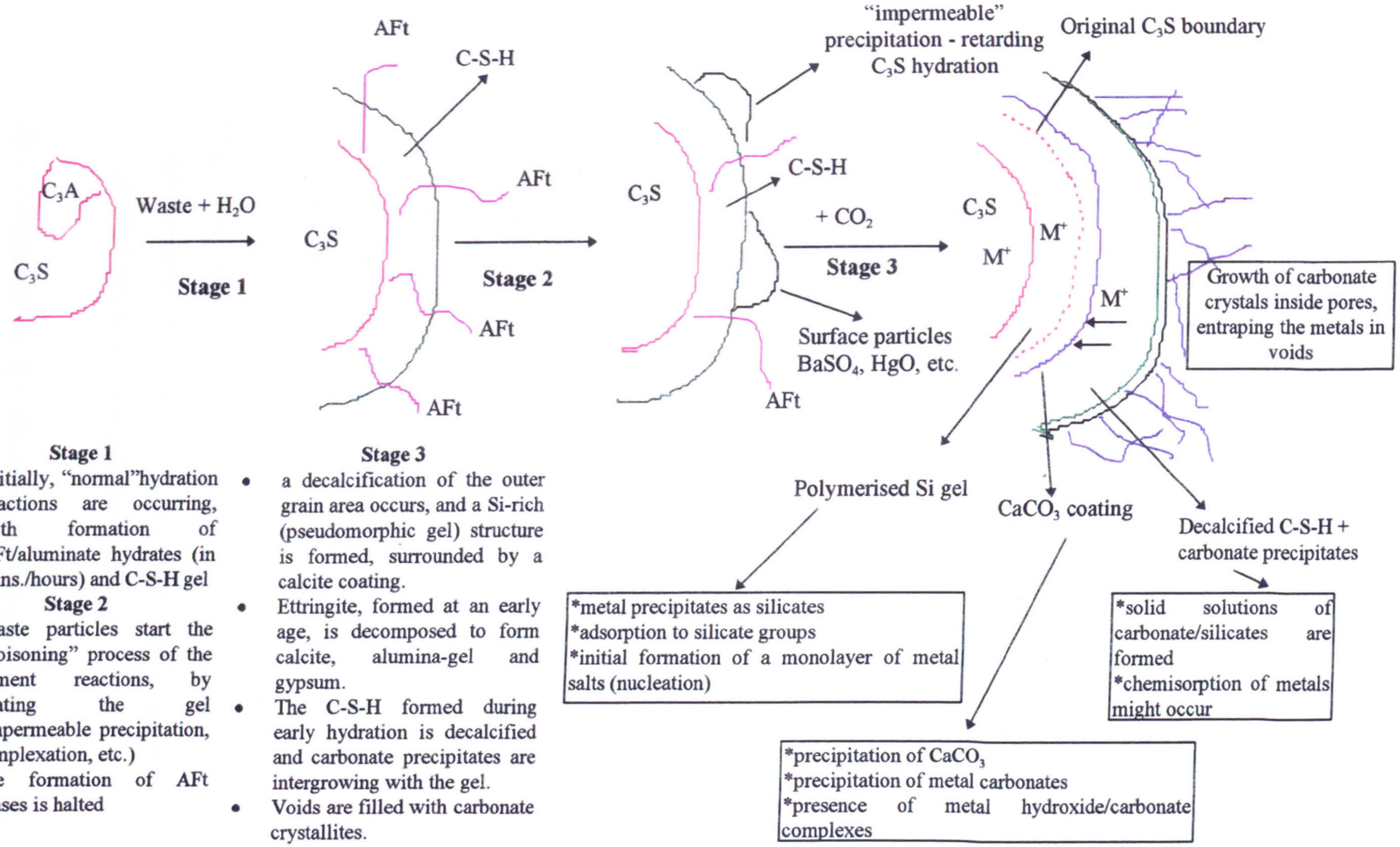
8.3.3 Leaching Characteristics

Leachate analysis gave significantly lower extraction results for carbonated specimens. The drop in pH values, after 24 hours extraction, was in average of 2-2.5 units and showed that, against all expectations, some metals were contained in the carbonated matrix, as a result of calcite precipitation, modifying pore structure and the precipitation of salts containing toxic species.

8.4 A MODEL FOR CARBONATED SOLIDIFIED WASTE PRODUCTS

Hydration reactions of cement are well described in the literature. Scrivener (1989) proposed a model for these reactions based on observations of cement hydration made with aid of an environmental cell situated in a scanning electron microscope. This model was further modified by Hills (1993) in an attempt to explain the effects of "poisoning" during solidification of certain wastes. Figure 8.1 is a schematic diagram showing the hydrated cement grain after carbonation. It is interesting to note that within only few minutes the carbonation reaction takes place, and consequently the entire modification on the solid assemblage occur.

Stage 1 represents the "normal" hydration described by Scrivener (1989), where she noted the appearance of hydration products within 10 minutes. A gelatinous layer was formed (C-S-H) around the C_3S grain, and eventually other hydration products, such as AFt, were located on the surface of this gel.



Stage 1

- Initially, "normal"hydration reactions are occurring, with formation of AFt/aluminate hydrates (in mins./hours) and C-S-H gel

Stage 2

- Waste particles start the "poisoning" process of the cement reactions, by coating the gel (impermeable precipitation, complexation, etc.)
- The formation of AFt phases is halted

Stage 3

- a decalcification of the outer grain area occurs, and a Si-rich (pseudomorphic gel) structure is formed, surrounded by a calcite coating.
- Ettringite, formed at an early age, is decomposed to form calcite, alumina-gel and gypsum.
- The C-S-H formed during early hydration is decalcified and carbonate precipitates are intergrowing with the gel.
- Voids are filled with carbonate crystallites.

Figure 8.1: Schematic diagram of a carbonated cement/waste matrix

Stage 2 illustrates the "poisoning" effects of waste particles during normal hydration. The production of AFt was basically halted and the gel membrane modified (Uchikawa et al., 1992; Hills, 1993) making it "impermeable" to normal hydration reactions.

The stage 3 shows the effects of carbonation upon the C_3S grain. It is interesting to note that considerable modification to the matrix happened in 10-20 minutes. The outer part of the C_3S grain becomes decalcified, leading to a polymerised silica-gel rim. This Si-rich rim is enveloped in a $CaCO_3$ layer in a decalcified C-S-H matrix with calcite precipitates. The metallic waste components are found to be physically and chemically entrapped within the system.

8.5 MAJOR CONTRIBUTIONS OF THIS WORK FOR SOLIDIFICATION TECHNOLOGY INDUSTRY

For more than 20 years solidification processes have been used to treat industrial and radioactive waste. Despite extensive application and considerable research, there is still areas that could benefit from additional work. A better understanding of solidification mechanisms, interferences, leaching behaviour and long-term performance would all help to improve process effeciency and increase public confidence in the technology.

Carbonation of solidified wastes could significantly enhance conventional hydraulic waste/cement processes under certain conditions. It is believed that this work made four major contributions to the area. They are:

1) an assessment of the effects of natural and accelerated carbonation on the development of mechanical, microstructural and chemical properties of solidified products using industrial wastes.

2) a comparison of the influence of different binders on the properties of carbonated solidified waste forms.

3) a practical evaluation of the kinetics of accelerated carbonation for different waste/binder systems.

4) the development of new model of possible mechanisms by which accelerated carbonation is involved in the fixation of metals during the solidification processes.

However, further research studies are essential in a number of areas. Some of these areas are outlined below in section 8.6.

8.6 RECOMMENDATIONS FOR FURTHER WORK

The following topics are suggested as requiring further work:

a) *Long-term performance*. The long-term performance of the carbonated waste is still obscure. In this work, results were based on 28 days age samples, and the evaluation of metal fixation was carried out using a static leaching test (water as leachate). Therefore, the need to assess the carbonated specimens in a long-term run is fundamental, and perhaps in parallel new test procedures need to be developed to evaluate this property, such as more severe and realistic leaching test.

b) *Carbonation studied on a field scale*. The use of carbonation in this study needs to be scaled up, i.e., studied from bench scale to field scale. Variables such as carbon dioxide flow rate, mix parameters (binder type, moisture content), material storage as well as taken into account the outdoor elements (landfill conditions, etc.) all may affect the success of the carbonated materials in a long-term process.

c) *Binder types*. Additional proprietary binders should be evaluated with respect to carbonation and perhaps a "generic" formulation could be developed for the process.

d) *Waste types*. In this study, metallic wastes were the only toxic waste explored, therefore, carbonation still need to be investigated in the presence of other inorganic wastes (radioactive waste, etc.) and organic wastes (volatile organic contaminants, etc.)

e) *Porosity, gas permeability, compaction tests*. In this work, moisture content was found to be a fundamental parameter for the process of carbonation, showing to be

directly related to porosity, and consequently, gas permeability. However, tests to assess these properties were not carried out, and it is believed that their relationships are fundamental to ensure that optimum moisture content is achieved, to form a stable and suitable product for waste encapsulation.

f) *Mechanisms of metal fixation during carbonation.* Several chemical features were shown to be responsible of toxic waste immobilisation during carbonation of waste materials. The mechanisms which give rise to these features need further exploration to form a quantitative basis that ultimately would explain metal diffusion.

CHAPTER 9

CONCLUSIONS

9.1 Most of the waste produced in the UK is sent to landfill for disposal without treatment. However, new EC legislation and important laws such as Environmental Protection Act of 1990 and 1995 as well as Landfill Tax Regulations are encouraging industries to pre-treat their waste prior to landfill.

9.2 Cement-based solidification has been established for more than 20 years, and OPC is commonly used. However, the presence of potentially deleterious chemical compounds has been shown to adversely affect cement matrices, compromising the performance of the solidified wastes.

9.3 Carbonation is known as a ubiquitous feature for Portland cement-based materials. However, the effects of carbonation have not been explored in great detail in solidification technology, hitherto, and this form the main objective of this work.

9.4 The effects of carbonation on a OPC/industrial waste product have clearly shown that physical and chemical changes in microstructure occurred. The solidified product was characterised by enhanced calcite contents, higher strength values (up to 70% for certain mixes) and a significant reduction in leachable metals extracted (up to 80% for certain mixes) when compared to samples cured in nitrogen or under normal atmospheric conditions.

9.5 The type of binder used also has a considerable influence on the degree of carbonation and the concentration of metals that can be immobilised. Calcite formation was found to be more abundance in C_3S-rich binders, such as RHPC and WOPC. On the other hand, the presence of mineral admixtures induced a decrease in the amount of calcite.

9.6 The quantity of carbon dioxide absorbed by different waste/binder systems was determined, allowing degree of carbonation fields' to be defined.

9.7 Carbon dioxide uptake was found to generally decrease with an increase in w/c ratio.

9.8 Cement pastes blended with industrial wastes reacted with carbon dioxide in greater proportions than cement paste only, showing the increased susceptibility of metal-doped pastes to carbonation. The following reactivity order was found: OPC>SRPC>WOPC.

9.9 Distinct mechanical and microstructural effects were found for the industrial wastes, showing the importance of considering antagonistic and synergistic effects of complex mixtures, which interfere with hydraulic reactivity of the carbonated binder system.

9.10 Solidified products carbonated under controlled carbonation conditions exhibit enhanced chemical and physical qualities.

9.11 Despite the complexity of the industrial wastes, the SEM results indicated an association between metals, calcite precipitates and the silica-rich rims found to surround the clinker grain particles.

9.12 SEM analysis confirmed an acceleration of C_3S hydration, with de-calcification of hydrated rims of cement grain and dense calcite precipitate infilling the porosity after carbonation. Also some micro-cracking were observed.

9.13 Certain metals appeared to be selectively incorporated either on the silica-rich rims or in the calcite/modified C-S-H matrix. Microprobe analysis showed that Cd and Ni were preferentially located in the decalcified C-S-H/calcite area, while Zn and Pb could be found also in the Si-rich rim.

9.14 FTIR and ^{29}Si NMR analysis have shown that there is an increased degree of polymerisation of the silicate hydrates and the presence of silanol groups, indicating the precipitation of metals as silicates.

9.15 ^{27}Al NMR showed that during carbonation octahedral Al formed on the hydration process was converted back to tetrahedral Al and a possible three dimensional network of a mixed AlO_4/SiO_4 structure has occurred.

9.16 A model has been proposed to illustrate the mechanisms responsible for metal fixation during carbonation.

The major contribution of this work to solidification technology arises from the investigation of the effects of carbonation on mechanical, chemical and microstructural properties of cement-based solidified waste products. The essential novel features of the study are concerned with the exploration of accelerated carbonation as a process assisting metal bearing wastes that would be difficult to treat by other means.

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APPENDIX A

INTRODUCTION

This Appendix provides the interactive Basic program for estimation of the total uptake of CO_2 from waste/binder specimens.

```
'This program reads games port located at &H201 to determine if opto switches
'are high or low (TTL).
'The assumption is that if both are high the port reads 252
'                    Channel 1 is high port reads 236
'                    Channel 2 is high port reads 220
'                  if both are low  the port reads 204
'
'The program is crude in that extensive use is made of variables.
DECLARE SUB STATUS (A1%, B1%)
DECLARE SUB GETINFO (A1$, A2$(), ATemp, APressure, AACratio, AWCratio, AMortarwt,
BTemp, BPressure, BACratio, BWCratio, BMortarw)
DECLARE SUB DUMPandCALCS (N%, A3$(), ATemp, APressure, AACratio, AWCratio,
AMortarwt, BTemp, BPressure, BACratio, BWCratio, BMortarw)

 COMMON SHARED Blank$, Acolor%, Bcolor%, Defaultcolor%, Infocolor%, Calccolor%
 DIM Ainfo$(20)
 DIM Binfo$(20)

'Define a few useful variables
Delay = .2       ' This is essentially  a debounce timer
Blank$ = "                                                                "
Ainfo$(0) = "A"
Binfo$(0) = "B"
Acolor% = 10'          Light green
Bcolor% = 11'          Light red
Defaultcolor% = 7'     White
Infocolor% = 9'        Light blue
Calccolor% = 12'       Light red as a warning that these are calculated


 CLS
 COLOR Infocolor%
 PRINT "For your assistance these are the existing data files"
 PRINT
 SHELL "cd C:\concrete"
 SHELL "dir/w"

 PRINT "Enter any key to continue"
 PRINT
 WHILE LEN(INKEY$) < 1: WEND
 CLS : COLOR Defaultcolor%' default to low luminosity white


 DO     'Use this loop to exit program  "Eflag%=1"

 'Notes to user
 COLOR Infocolor%
 LOCATE 1, 1
```

```
PRINT "DON'T RUN OVER MIDNIGHT:Keystrokes are NOT case sensitive"
LOCATE 2, 1
PRINT "A/B to start/stop log Ch A/B to disc: E to exit program if A/B are not logging"
COLOR Defaultcolor%

'Define a few more variables
Aflag% = 0: Bflag% = 0: Eflag% = 0


DO     'Start of data taking loop Aflag% or Bflag% or Q$=""
CALL STATUS(Astatus%, Bstatus%)
Apaststatus% = Astatus%
Bpaststatus% = Bstatus%
 Startpause = TIMER: WHILE TIMER < Startpause + Delay: WEND
 Q$ = INKEY$

 'Check keyboard and activate/deactivate Ch A
 IF ((Q$ = "A" OR Q$ = "a") AND Aflag% = 0) THEN
            Channel$ = "A"
            CALL GETINFO(Channel$, Ainfo$(), ATemp, APressure, AACratio, AWCratio,
              AMortarwt, BTemp, BPressure, BACratio, BWCratio, BMortarw)
            Aflag% = 1
            NA% = 0
  ELSEIF Q$ = "" AND Aflag% = 1 THEN
            CALL STATUS(Astatus%, Bstatus%)
            IF (Astatus% = 1) AND (Apaststatus% = 0) THEN
                NA% = NA% + 1
                CALL DUMPandCALCS(NA%, Ainfo$(), ATemp, APressure, AACratio, AWCratio,
                 AMortarwt, BTemp, BPressure, BACratio, BWCratio, BMortarw)
          END IF
ELSEIF ((Q$ = "A" OR Q$ = "a") AND Aflag% = 1) THEN
          CLOSE #1          'Close the data file for Ch A output with label #1
          SHELL "cd\dos"
          Cmd$ = "attrib +r " + Ainfo$(1)
          SHELL Cmd$
          SHELL "cd\concrete"
          COLOR Acolor%
          LOCATE 12, 1: PRINT Blank$: LOCATE 12, 1
          PRINT "Channel A file "; Ainfo$(1); " closed at "; TIME$
          COLOR Defaultcolor%
          Aflag% = 0
 END IF

     'Check keyboard and activate/deactivate Ch B
 IF ((Q$ = "B" OR Q$ = "b") AND Bflag% = 0) THEN
       Channel$ = "B"
       CALL GETINFO(Channel$, Binfo$(), ATemp, APressure, AACratio, AWCratio,
        AMortarwt, BTemp, BPressure, BACratio, BWCratio, BMortarw)
       Bflag% = 1
       NB% = 0
       Bflag% = 1
 ELSEIF Q$ = "" AND Bflag% = 1 THEN
       CALL STATUS(Astatus%, Bstatus%)

       IF (Bstatus% = 1) AND (Bpaststatus% = 0) THEN
            NB% = NB% + 1
```

```
            CALL DUMPandCALCS(NB%, Binfo$(), ATemp, APressure, AACratio, AWCratio,
             AMortarwt, BTemp, BPressure, BACratio, BWCratio, BMortarw)
        END IF
ELSEIF ((Q$ = "B" OR Q$ = "b") AND Bflag% = 1) THEN
        CLOSE #2            'Close the data file for Ch B output with label #2
        SHELL "cd\dos"
        Cmd$ = "attrib +r " + Binfo$(1)
        SHELL Cmd$
        SHELL "cd\concrete"
        COLOR Bcolor%
        LOCATE 22, 1: PRINT Blank$: LOCATE 22, 1
        PRINT "Channel B file "; Binfo$(1); " closed at "; TIME$
        COLOR Defaultcolor%
        Bflag% = 0
    END IF

    'Monitor Ch A and B but do not write to disc


    CALL STATUS(Astatus%, Bstatus%)
    LOCATE 23, 1
    COLOR Infocolor%
    PRINT "Astatus ;"; Astatus%, "Bstatus "; Bstatus%, TIME$
    COLOR Defaultcolor%

IF Aflag% = 1 THEN
      COLOR Acolor%
      LOCATE 12, 1: PRINT Blank$: LOCATE 12, 1
      PRINT "Channel A file "; Ainfo$(1); " running @ "; TIME$
      COLOR Defaultcolor%
END IF
IF Bflag% = 1 THEN
      COLOR Bcolor%
      LOCATE 22, 1: PRINT Blank$: LOCATE 22, 1
      PRINT "Channel B file "; Binfo$(1); " running @ "; TIME$
      COLOR Defaultcolor%
END IF

LOOP WHILE Aflag% OR Bflag% OR Q$ = ""  'End of data taking

IF (Q$ = "E" OR Q$ = "e") THEN Eflag% = 1

LOOP UNTIL Eflag%                   ' Exit program
CLS
CLOSE


END

SUB CHECKFILE (Errorflag%, FileID$)
Cmd$ = "dir *.dat >;c:\concrete\filelist.lst": SHELL Cmd$
OPEN "c:\concrete\filelist.lst" FOR INPUT AS #3
FileID$ = FileID$ + ".DAT"
'See if the file specified already exists
DO
Check$ = ""
INPUT #3, Check$
PRINT Check$
```

```
PRINT FileID$
IF Check$ = FileID$ THEN
        Errorflag% = 1
        PRINT "ERRRRRRRR", FileID$
        END IF
INPUT Q$
LOOP UNTIL EOF(3) OR Errorflag%

CLOSE #3

END SUB

SUB DUMPandCALCS (Npoints%, Info$(), ATemp, APressure, AACratio, AWCratio, AMortarwt,
BTemp, BPressure, BACratio, BWCratio, BMortarwt)
STATIC StartA
STATIC StartB
'Channel a first
IF Info$(0) = "A" THEN
COLOR Acolor%
        Temp = ATemp
        Pressure = APressure
        ACratio = AACratio
        WCratio = AWCratio
        Mortarwt = AMortarwt

        IF Npoints% = 1 THEN

                StartA = TIMER
                PRINT #1, DATE$
                PRINT #1, "Temperature Pressure ACratio WCratio Mortarwt"
                PRINT #1, Temp; ","; Pressure; ","; ACratio; ","; WCratio; ","; Mortarwt
        END IF


        'Correction factor for scale is 7/5
        MeasuredVol = Npoints% * 7 / 5
        VolumeSTP = (MeasuredVol * ((Pressure + 7) / 1013) / (1 + .0037 * Temp))
        MassCO2 = .00197 * VolumeSTP
        Cementwt = Mortarwt / (1 + ACratio + WCratio)
        PercentCO2 = 100 * MassCO2 / Cementwt
        LOCATE 11, 1: PRINT Blank$: LOCATE 11, 1
        COLOR Calccolor%
        PRINT "Ch A"; Npoints%, "%CO2 = "; PercentCO2, "Time elapsed = "; (TIMER - StartA) /
60
        PRINT #1, (TIMER - StartA) / 60; ","; Npoints%; ","; PercentCO2
COLOR Defaultcolor%
END IF
'Now channel B
IF Info$(0) = "B" THEN
COLOR Bcolor%
        Temp = BTemp
        Pressure = BPressure
        ACratio = BACratio
        WCratio = BWCratio
        Mortarwt = BMortarwt

        IF Npoints% = 1 THEN

                StartB = TIMER
```

```
        PRINT #2, DATE$
        PRINT #2, "Temperature Pressure ACratio WCratio Mortarwt"
        PRINT #2, Temp; ","; Pressure; ","; ACratio; ","; WCratio; ","; Mortarwt
    END IF


    'Correction factor for scale is 7/5
    MeasuredVol = Npoints% * 7 / 5
    VolumeSTP = (MeasuredVol * ((Pressure + 7) / 1013) / (1 + .0037 * Temp))
    MassCO2 = .00197 * VolumeSTP
    Cementwt = Mortarwt / (1 + ACratio + WCratio)
    PercentCO2 = 100 * MassCO2 / Cementwt
    COLOR Calccolor%
        LOCATE 21, 1: PRINT Blank$: LOCATE 21, 1
        PRINT "Ch B"; Npoints%, "%CO2 = "; PercentCO2, "Time elapsed = "; (TIMER - StartB) /
60
        PRINT #2, (TIMER - StartB) / 60; ","; Npoints%; ","; PercentCO2
    COLOR Defaultcolor%
    END IF

    END SUB

    SUB GETINFO (Chan$, Info$(), ATemp, APressure, AACratio, AWCratio, AMortarwt, BTemp,
    BPressure, BACratio, BWCratio, BMortarwt)
    IF Chan$ = "A" THEN
    COLOR Acolor% 'Light green for Channel A
        LOCATE 4, 1: PRINT Blank$: LOCATE 4, 1
        INPUT "Filename for Channel A, 8 characters or less, no extension"; Filename$
        Info$(1) = "C:\concrete\" + Filename$ + ".dat"
       LOCATE 5, 1: PRINT Blank$: LOCATE 5, 1
       PRINT "Enter the following variables;-"
        LOCATE 6, 1: PRINT Blank$: LOCATE 6, 1
       INPUT "Ch A Temperature (Centigrade) "; ATemp
        LOCATE 7, 1: PRINT Blank$: LOCATE 7, 1
       INPUT "Ch A Pressure    (mBar      ) "; APressure
        LOCATE 8, 1: PRINT Blank$: LOCATE 8, 1
       INPUT "Ch A Agg/Cem ratio           "; AACratio
        LOCATE 9, 1: PRINT Blank$: LOCATE 9, 1
       INPUT "Ch A Water/Cem ratio         "; AWCratio
        LOCATE 10, 1: PRINT Blank$: LOCATE 10, 1
       INPUT "Ch A Mortar weight (gms     ) "; AMortarwt
        LOCATE 11, 1: PRINT Blank$: LOCATE 11, 1' Clear this line in case there was a previous
run
        OPEN Info$(1) FOR OUTPUT AS #1          'Open the data file for Ch A output with label #1
    COLOR Defaultcolor%
    END IF
    IF Chan$ = "B" THEN
    COLOR Bcolor%
          LOCATE 14, 1: PRINT Blank$: LOCATE 14, 1
          INPUT "Filename for Channel B, 8 characters or less, no extension"; Filename$
          Info$(1) = "C:\concrete\" + Filename$ + ".dat"
           LOCATE 15, 1: PRINT Blank$: LOCATE 15, 1
          PRINT "Enter the following variables;-"
           LOCATE 16, 1: PRINT Blank$: LOCATE 16, 1
          INPUT "Ch B Temperature (Centigrade) "; BTemp
           LOCATE 17, 1: PRINT Blank$: LOCATE 17, 1
          INPUT "Ch B Pressure    (mBar      ) "; BPressure
           LOCATE 18, 1: PRINT Blank$: LOCATE 18, 1
           INPUT "Ch B Agg/Cem ratio           "; BACratio
```

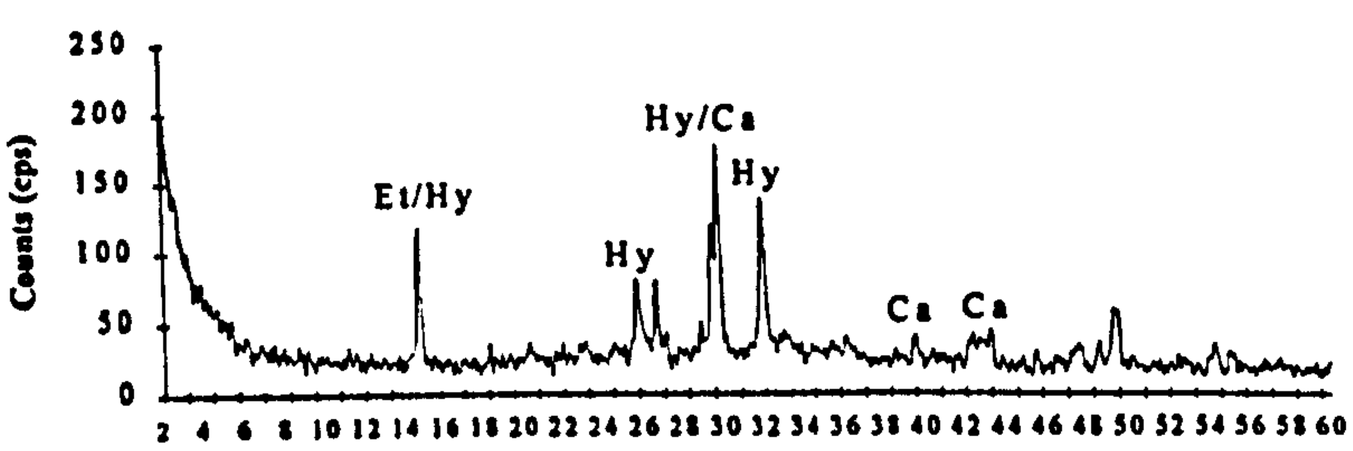
```
      LOCATE 19, 1: PRINT Blank$: LOCATE 19, 1
      INPUT "Ch B Water/Cem ratio          "; BWCratio
      LOCATE 20, 1: PRINT Blank$: LOCATE 20, 1
      INPUT "Ch B Mortar weight (gms     ) "; BMortarwt
      LOCATE 21, 1: PRINT Blank$: LOCATE 21, 1' Clear this line in case there was a previous
run
      OPEN Info$(1) FOR OUTPUT AS #2        'Open the data file for Ch B output with label #2
COLOR Defaultcolor%
END IF
END SUB

SUB STATUS (Astatus%, Bstatus%)
Presentstatus% = INP(&H201)
Bothfull% = 252
ChAfull% = 236
ChBfull% = 220
Bothlow% = 204
IF Presentstatus% = Bothfull% THEN
      Astatus% = 1
      Bstatus% = 1
ELSEIF Presentstatus% = Bothlow% THEN
      Astatus% = 0
      Bstatus% = 0
ELSEIF Presentstatus% = ChAfull% THEN
      Astatus% = 1
      Bstatus% = 0
ELSEIF Presentstatus% = ChBfull% THEN
      Astatus% = 0
      Bstatus% = 1
ELSE
      BEEP
      CLS
      CLOSE
      PRINT "INVALID BYTE HAS BEEN READ ON &H201 (GAMES PORT)"
      PRINT "CHECK CONNECTIONS etc."
      PRINT "BYTE VALUE IS "; "HEX"; Presentstatus%
      PRINT "PROGRAM TERMINATED"
      PRINT "ANY OPEN FILES HAVE BEEN CLOSED"
      BEEP
      END
END IF


END SUB
```

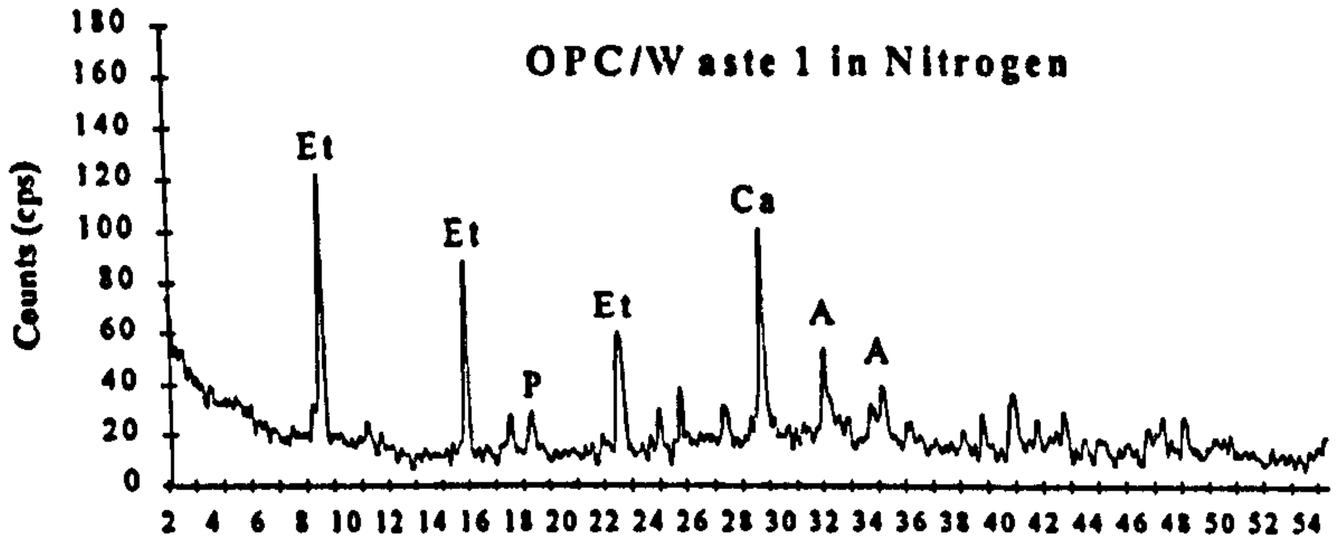
APPENDIX B

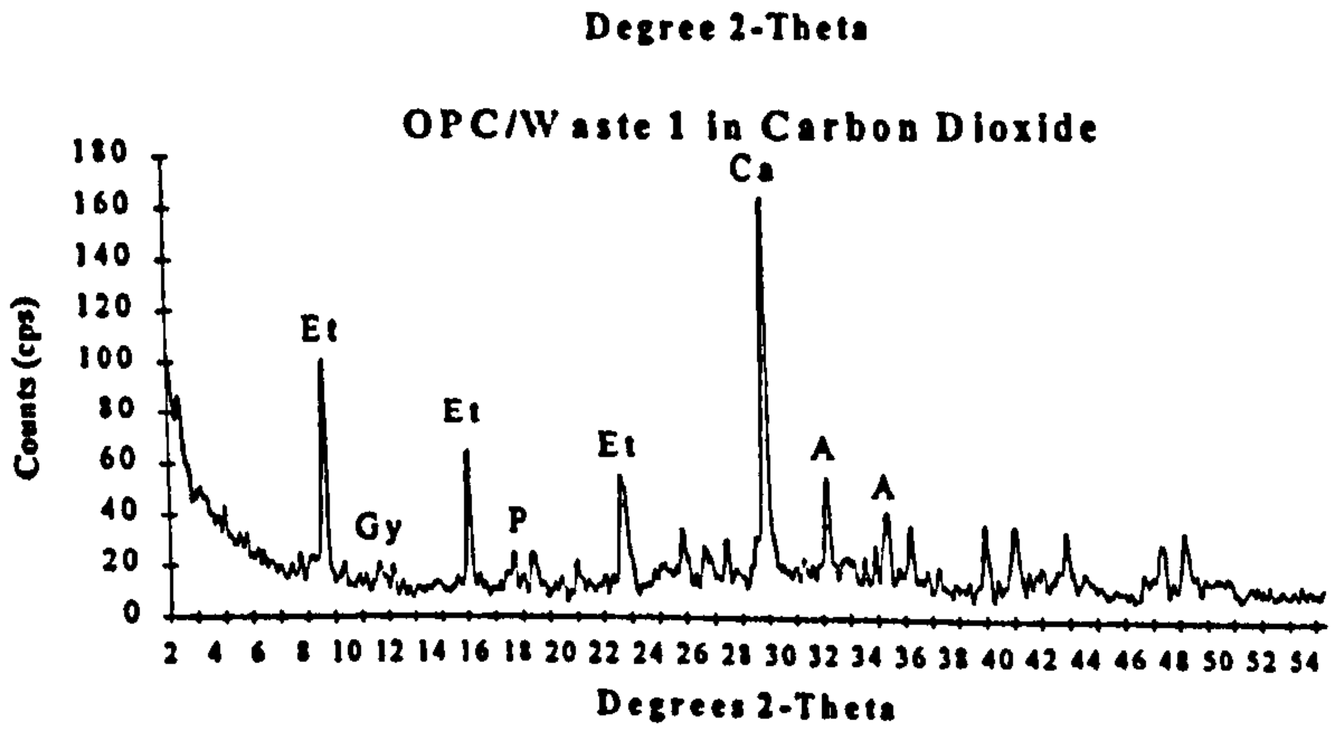
INTRODUCTION

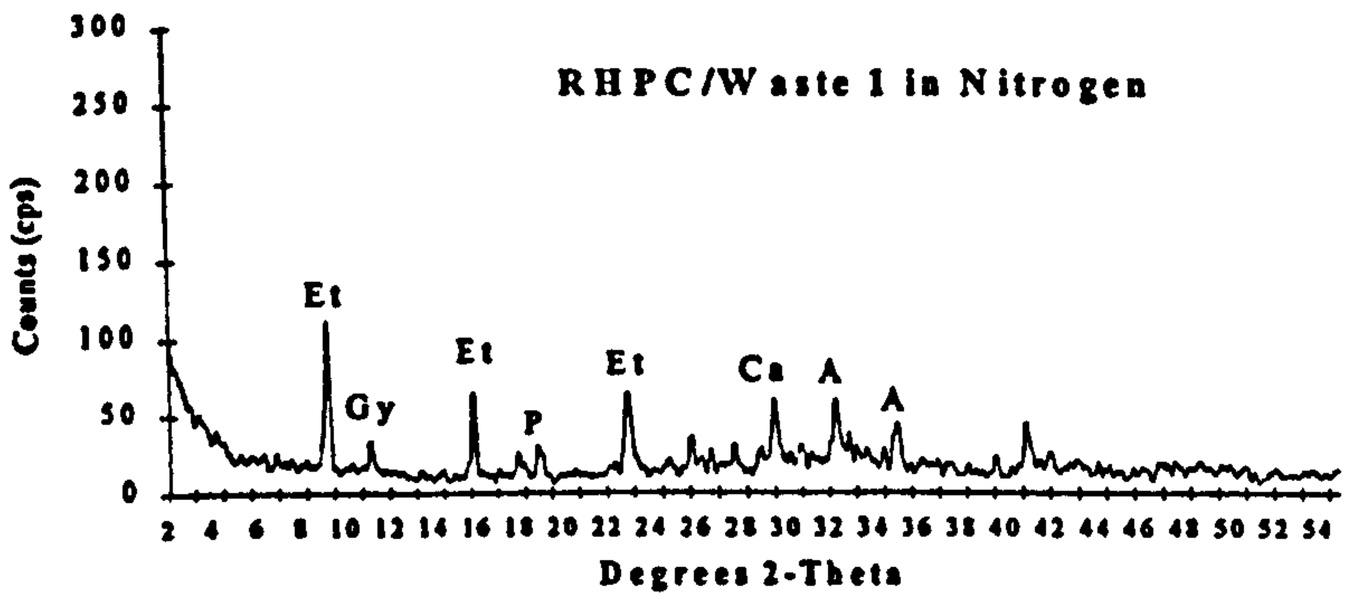
This Appendix gives the x-rays diffraction patterns and leachate metal concentration results which complement the observations made during the study of the effects of carbonation on properties of blended and non-blended cement solidified waste forms (Chapter 4).

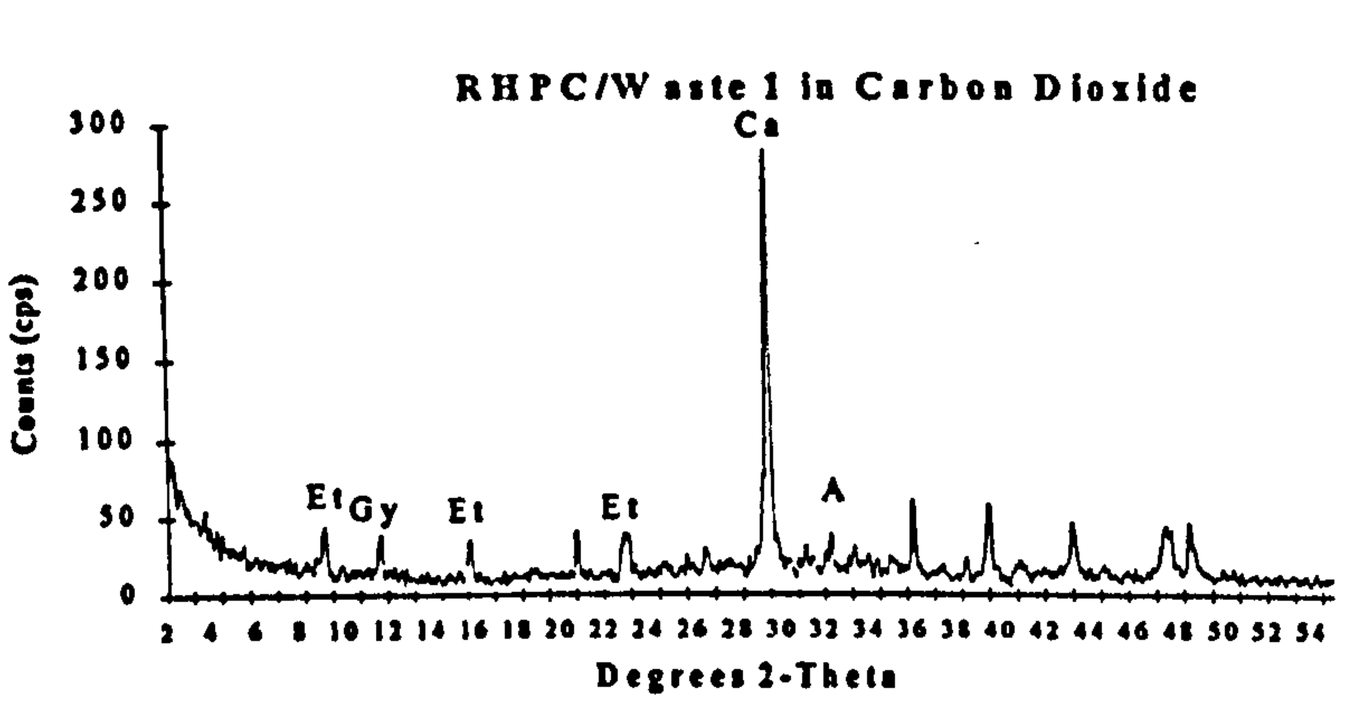
The x-rays diffraction patterns for specimens containing industrial wastes solidified with five different hydraulic binders (OPC, RHPC, SRPC, WOPC, CAC) are shown in Figure B.1. Tables B.1 and B.2 give the summary data for the main crystalline phases of the raw waste and the solidified waste products. The leachate metal concentrations for all waste/cement systems (blended and non-blended) are given in Tables B.3 and B.4.

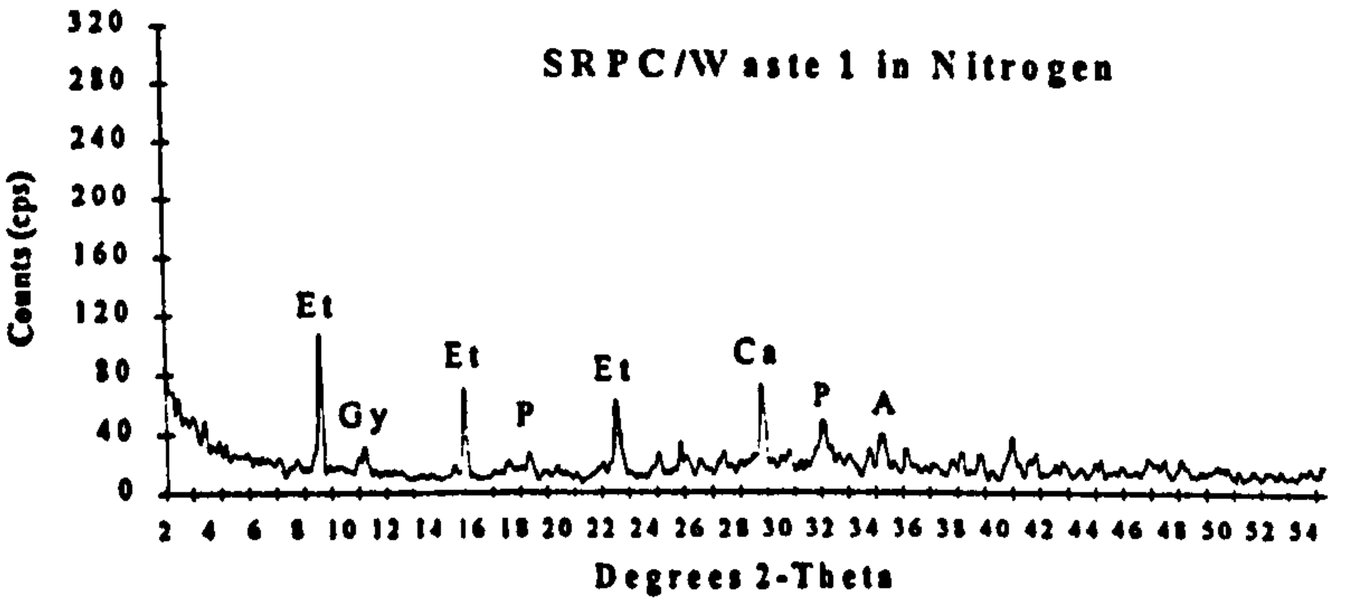


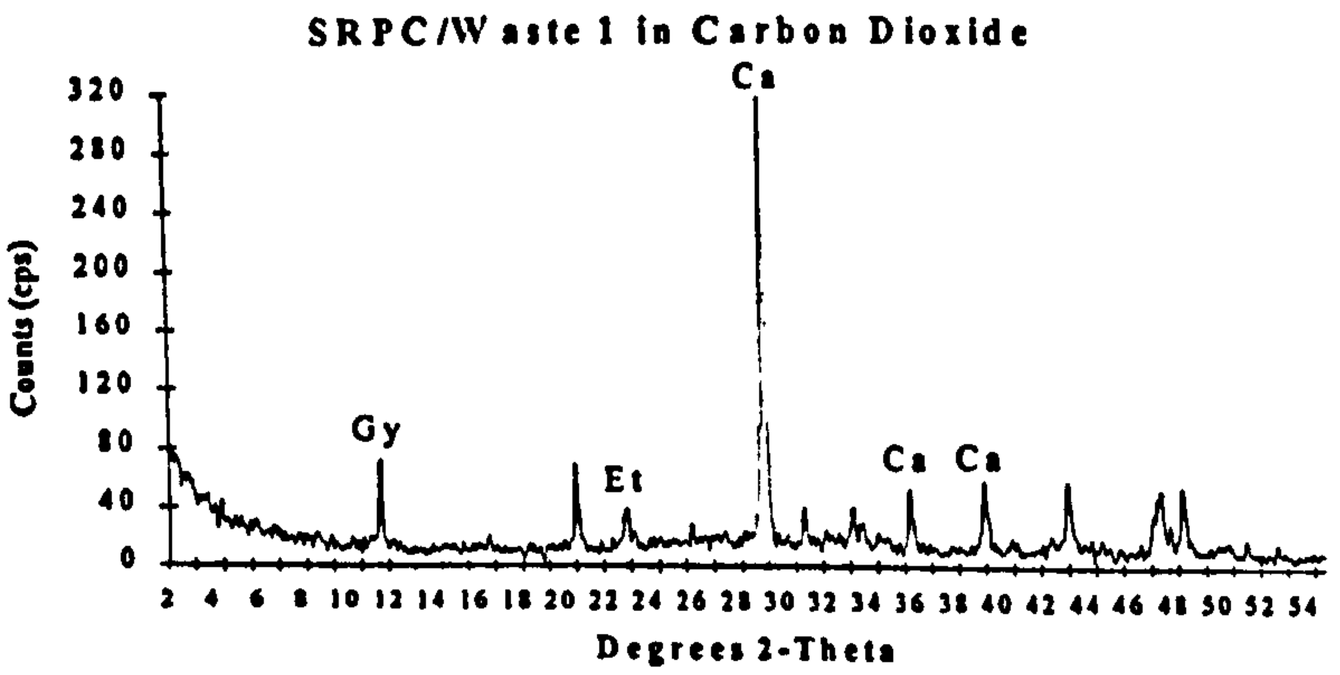


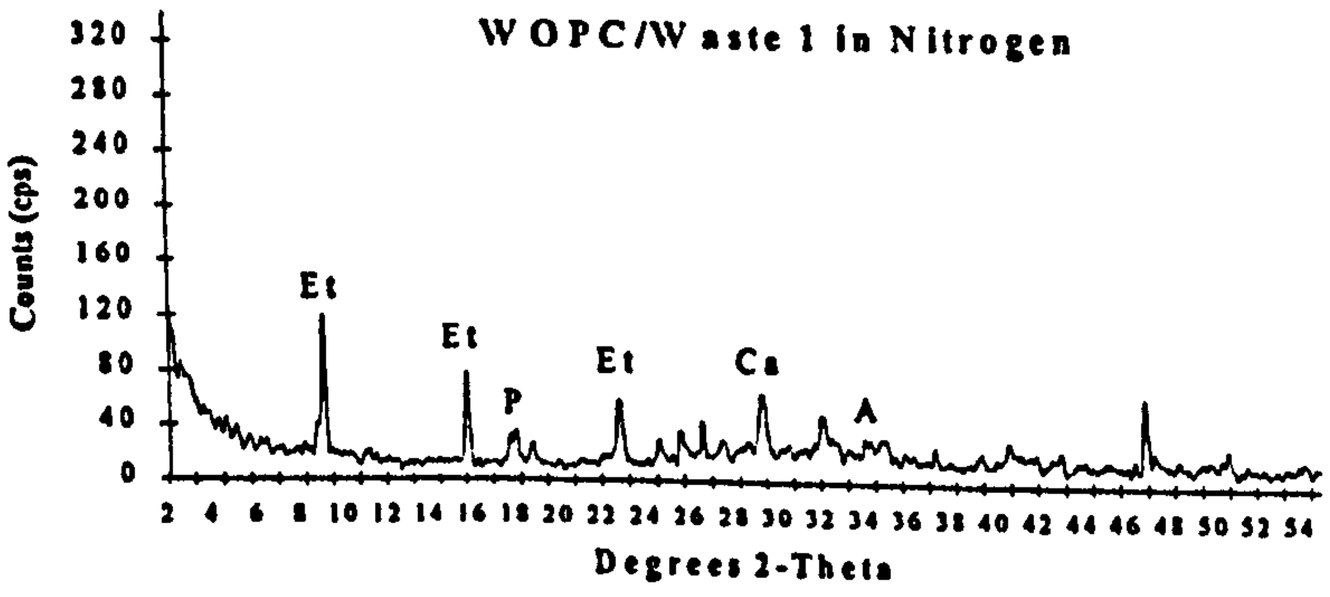


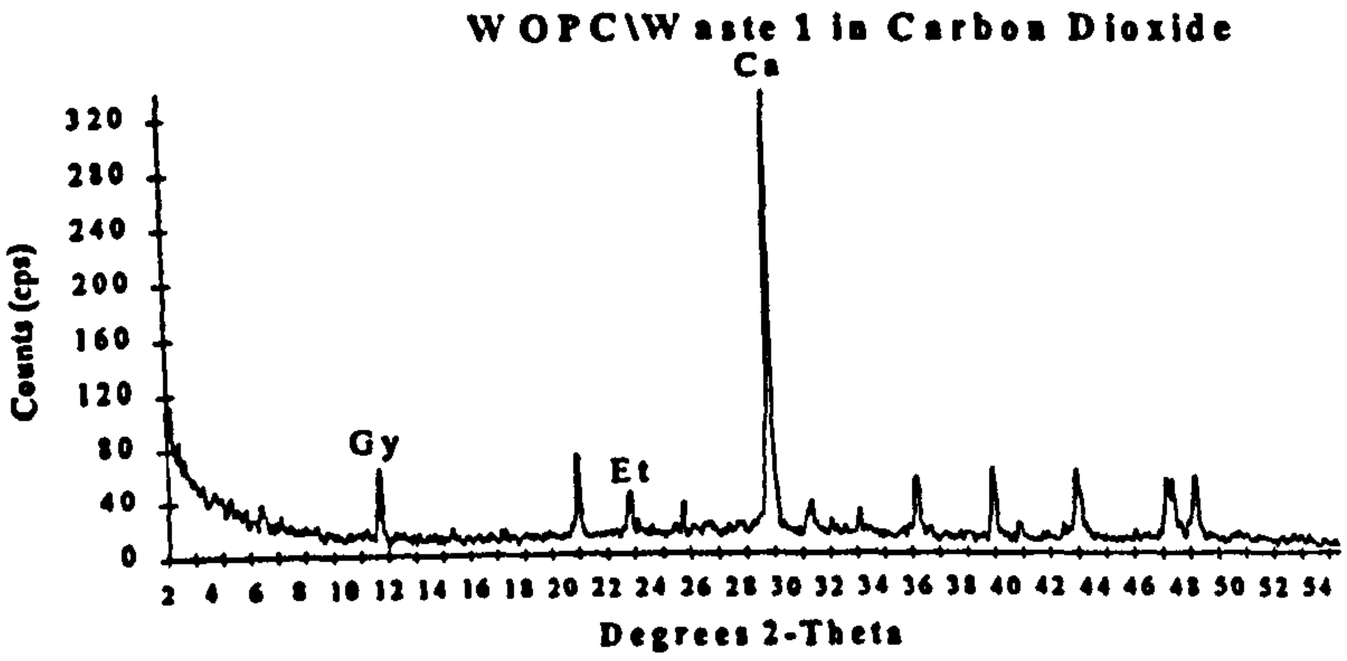

RHPC/Waste 1 in Nitrogen
Counts (cps)
Degrees 2-Theta
Et
Gy
Et
P
Et
Ca
A
A

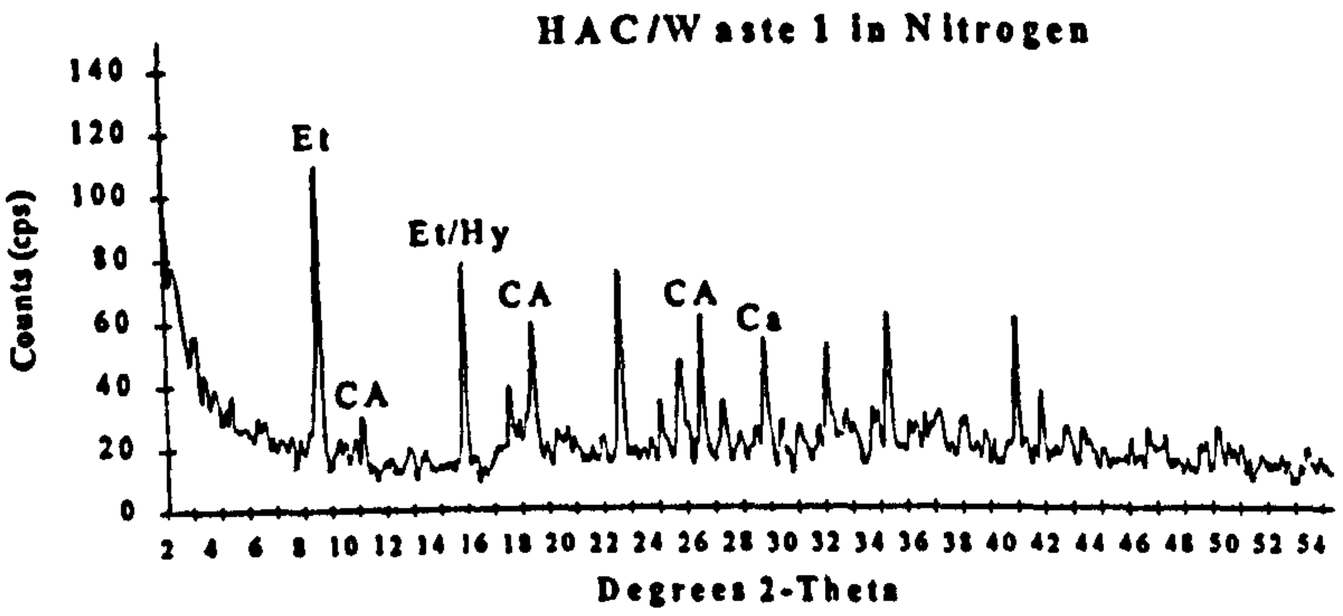

RHPC/Waste 1 in Carbon Dioxide
Counts (cps)
Degrees 2-Theta
Ca
Et
Gy
Et
Et
A

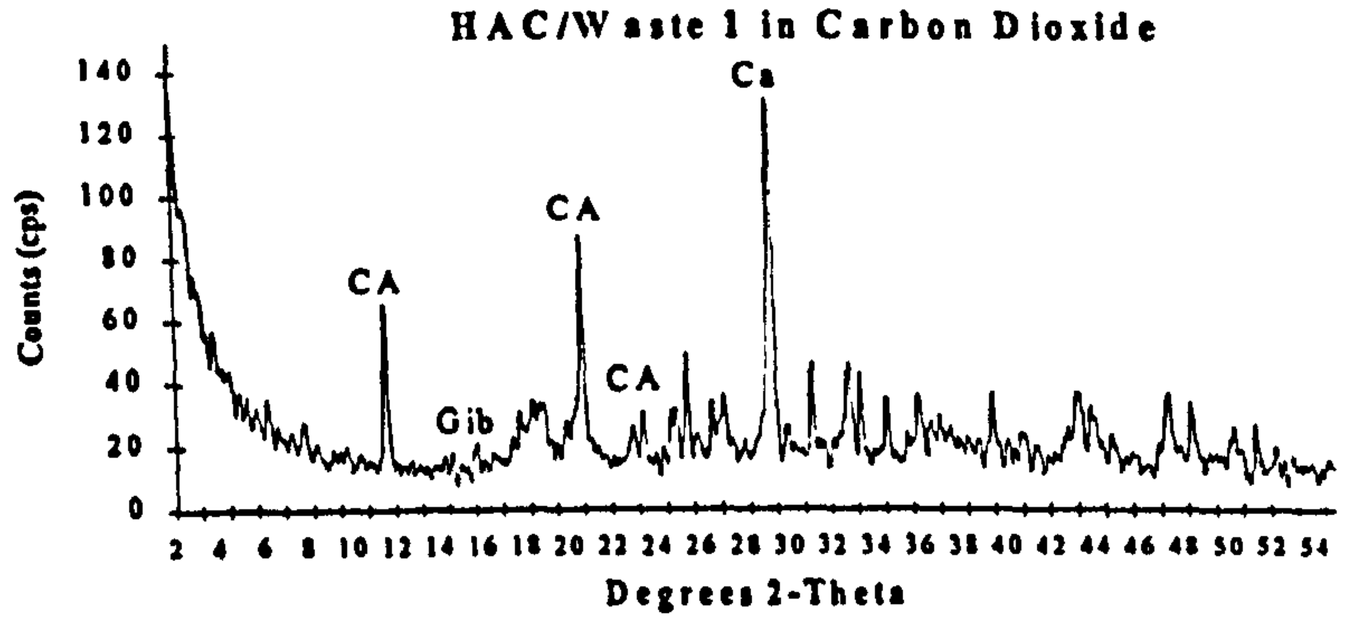

SRPC/Waste 1 in Nitrogen
Counts (cps)
Degrees 2-Theta
Et
Gy
Et
P
Et
Ca
P
A

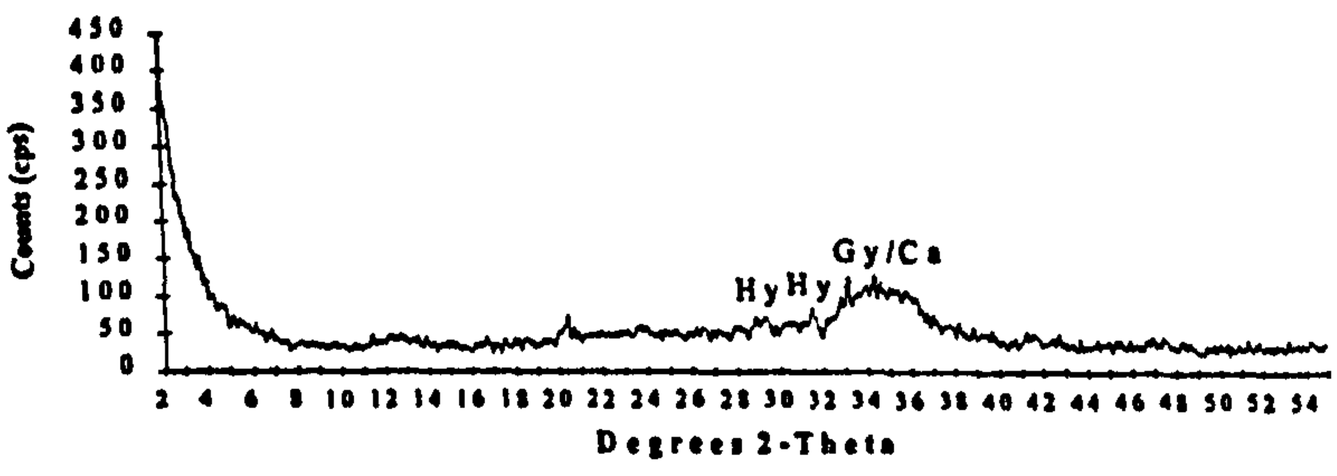

SRPC/Waste 1 in Carbon Dioxide
Counts (cps)
Degrees 2-Theta
Ca
Gy
Et
Ca
Ca

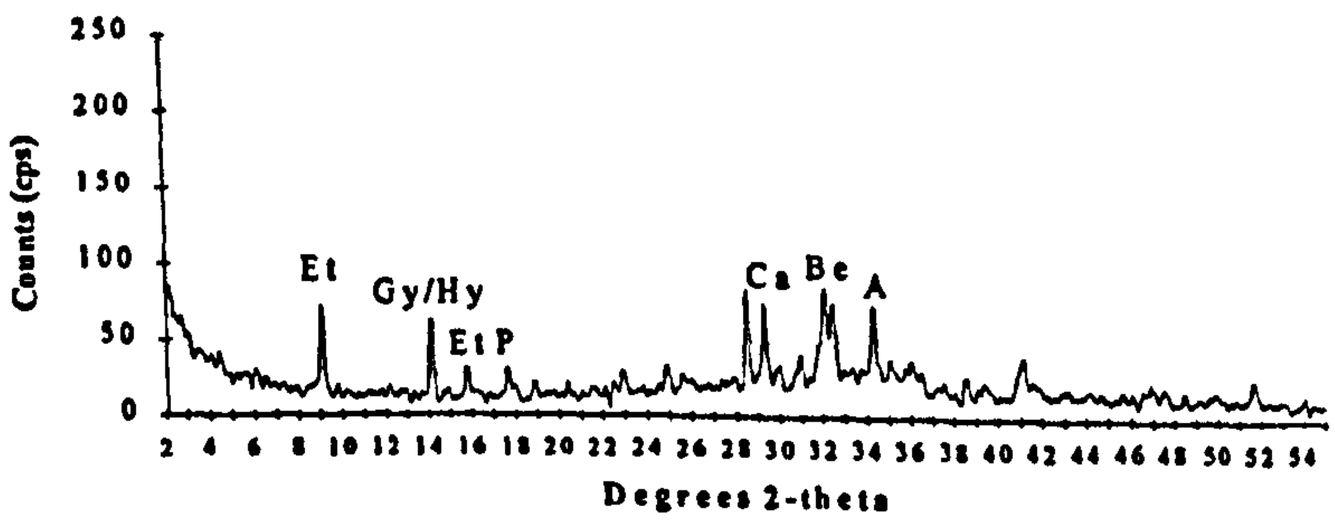

WOPC/Waste 1 in Nitrogen
Counts (cps)
Degrees 2-Theta
Et
Et
P
Et
Ca
A


W OPC\W aste 1 in Carbon Dioxide
Counts (cps)
320
280
240
200
160
120
80
40
0
Ca
Gy
Et
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54
Degrees 2-Theta

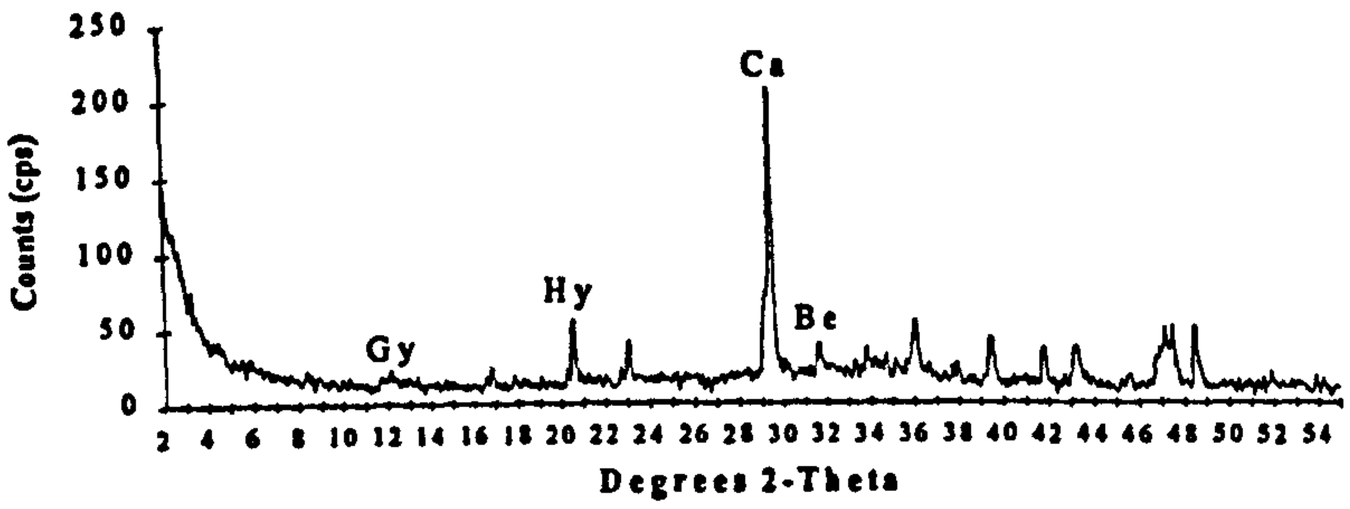

HAC/W aste 1 in Nitrogen
Counts (cps)
140
120
100
80
60
40
20
0
Et
Et/Hy
CA
CA
Ca
CA
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54
Degrees 2-Theta


HAC/W aste 1 in Carbon Dioxide
Counts (cps)
140
120
100
80
60
40
20
0
Ca
CA
CA
CA
Gib
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54
Degrees 2-Theta

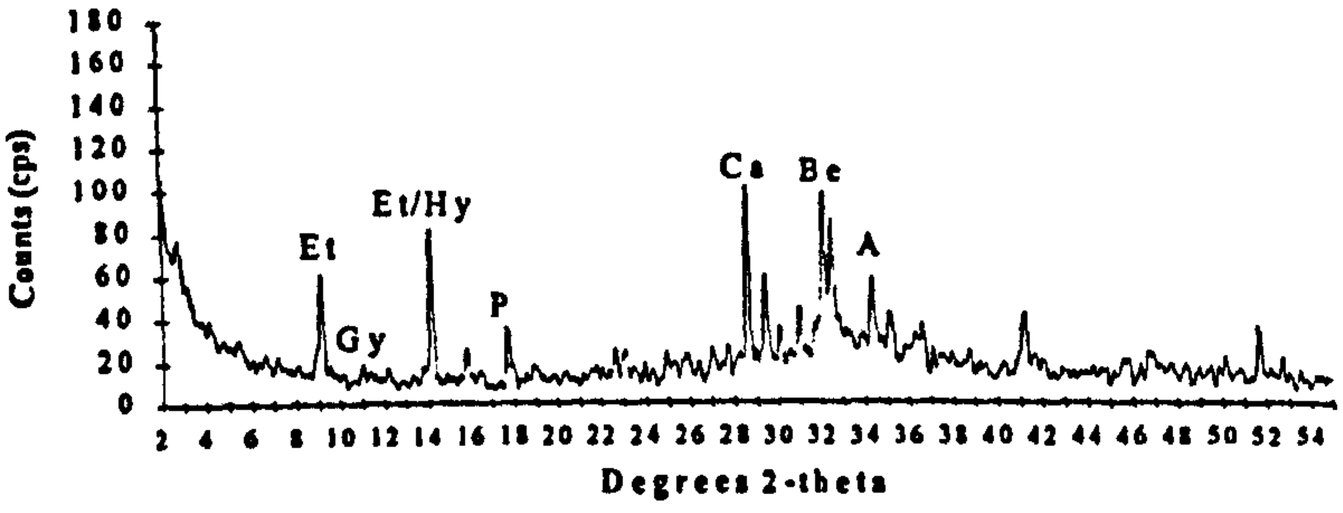

Dried Raw W aste 2
Counts (cps)
450
400
350
300
250
200
150
100
50
0
Gy/Ca
Hy Hy
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54
Degrees 2-Theta


OPC/W aste 2 in Nitrogen
Counts (cps)
250
200
150
100
50
0
Et
Gy/Hy
Et P
Ca
Be
A
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54
Degrees 2-theta

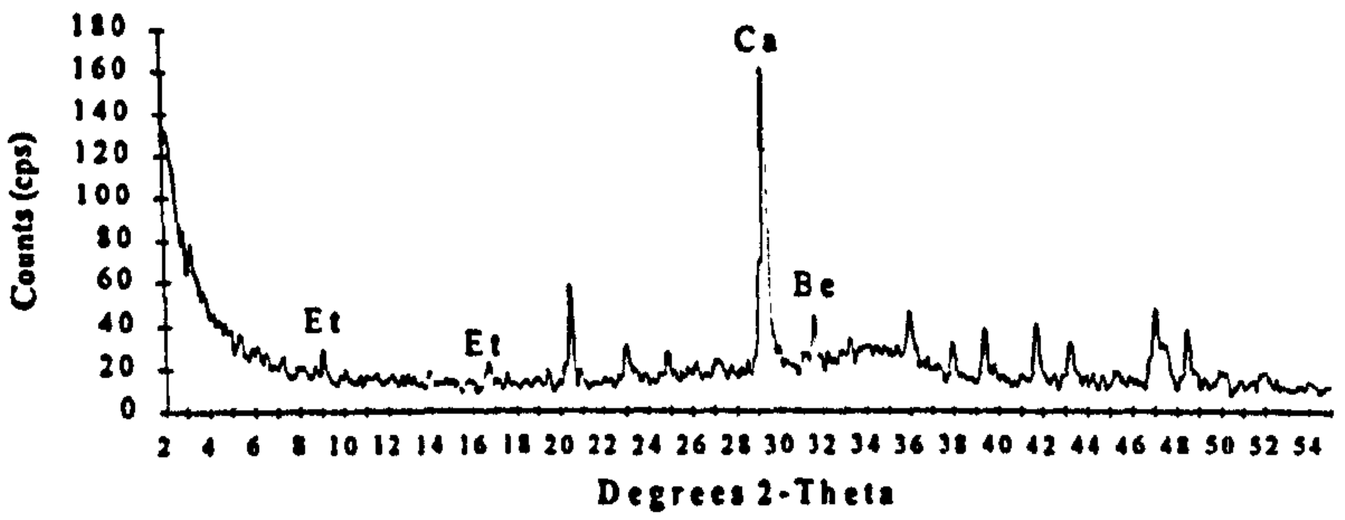
OPC/Waste 2 in Carbon Dioxide



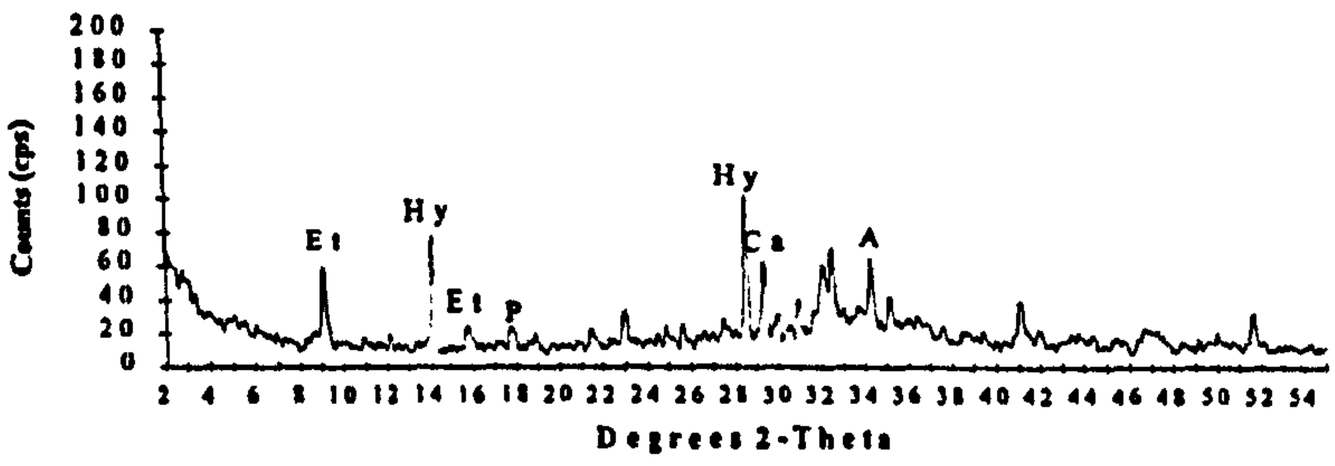
RHPC/Waste 2 in Nitrogen



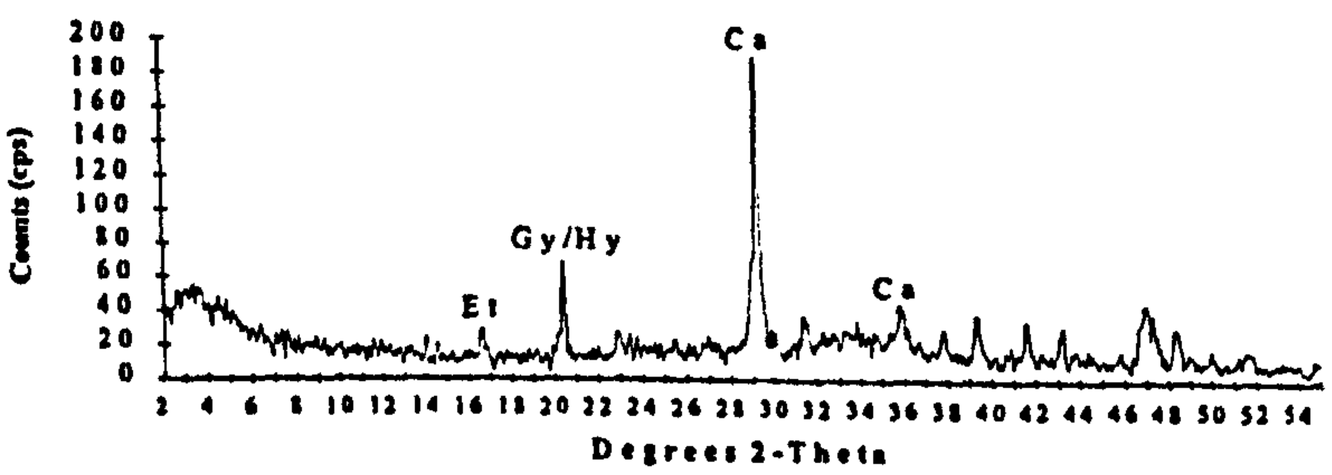
RHPC/Waste 2 in Carbon Dioxide



SRPC/Waste 2 in Nitrogen



SRPC/Waste 2 in Carbon Dioxide



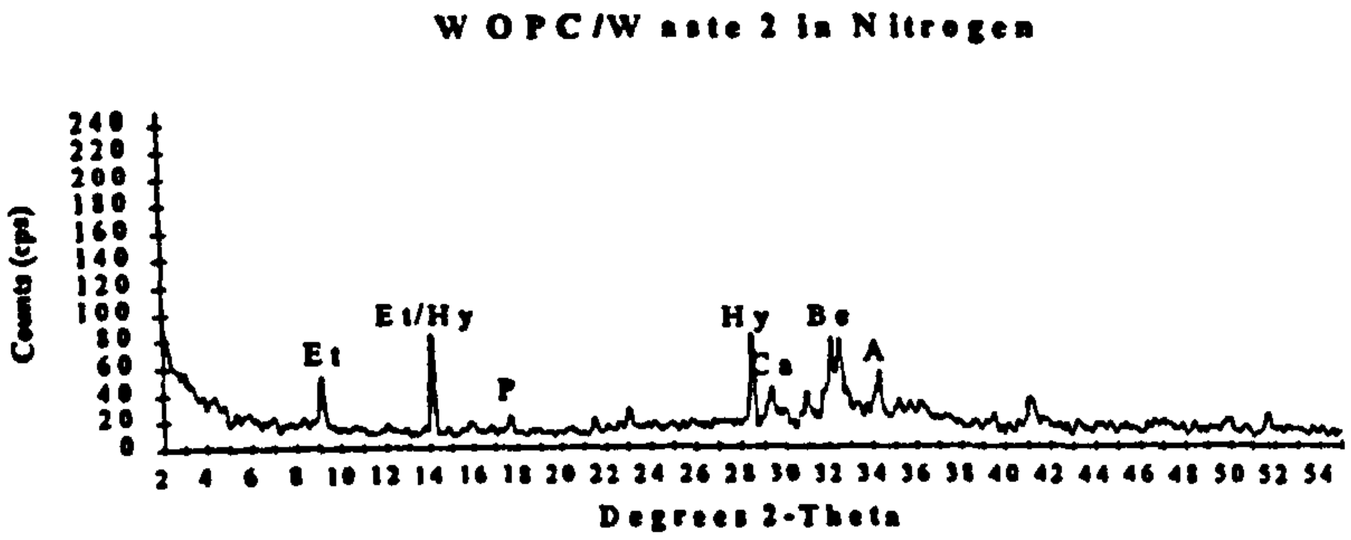


Figure B.1: Qualitative X-Ray Diffractograms, where: Et= ettringite; Gy= gypsum ; A= alite; Be= belite; P= portlandite; Ar= aragonite; Ca= calcite; CA= calcium aluminate phases; Hy= hemihydrate; Gib= gibbsite

Table B.1: Summary table of X-ray data for the main crystalline phases of the raw dried industrial wastes

Waste/Phase	2-theta (degrees)	D-spacing (Ångstrom)	Relative Intensity (I/Imax)
Cory Waste			
hemihydrate/anhydrite	14.73	6.03	56
hemihydrate	25.69	3.74	32
hemihydrate/calcite	29.43	3.04	60
hemihydrate	29.71	3.01	100
hemihydrate	31.9	2.81	33
Metal Colour Waste			
hemihydrate	29.45	3.04	100
hemihydrate	31.69	2.82	76
gypsum/calcite	33.0 - 39.0	2.71 - 2.31	<60

Table B.2: Summary table of X-ray data for solidified wastes

Mineral	2-theta (degrees)	D-spacing (Ångstrom)	Relative Intensity (I/Imax)
Portlandite	18.1	4.90	70
	34.2	2.63	100
	28.5	1.80	40
C_3S	32.7	2.76	100
	34.5	2.60	100
C_2S	32.2	2.80	21
C_3A	33.1	2.7	100
CAH_{10}	6.2	14.3	100
	12.45	7.16	100
	25.0	3.56	70
Gibbsite	18.41	4.83	100
	20.46	4.34	40
Calcite	29.43	3.04	100
Aragonite	26.24	3.40	100
Ettringite	9.2	9.8	100
	15.8	5.61	80
	22.7	3.88	90
Gypsum	11.71	7.56	100

Table B.3 : Leachate metal concentrations for waste 1 specimens (mg/L)

Waste 1 or Cory Waste Specimens

Metals	Environ.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	CO_2	3.3	5.3	6.0	2.7	3.3	9.3	12.0	3.3	11.3	4.6	8.0	2.2	6.0	5.6	6.0
Cr	Air	8.6	14.0	19.3	13.3	7.3	11.3	17.3	7.3	12.6	6.6	11.5	6.7	8.6	8.7	8.0
	N_2	28.6	29.3	26.6	17.3	8.6	24.6	29.9	19.3	21.9	11.3	12.8	8.0	15.3	12.2	9.9
	CO_2	<0.1	0.7	0.7	0.7	0.6	1.3	2.7	0.7	3.3	1.3	2.6	1.3	2.0	1.3	2.6
Cu	Air	2.0	2.0	1.3	2.2	0.7	2.0	0.7	1.3	3.6	1.3	3.0	0.7	2.1	1.3	3.1
	N_2	3.3	3.3	2.7	2.0	1.3	3.3	4.0	5.3	7.3	2.7	5.2	2.0	4.6	3.3	4.9
	CO_2	<0.1	1.3	0.7	0.7	0.6	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.7	0.7	1.9
Ni	Air	0.7	2.9	2.0	2.0	2.0	2.7	2.7	1.3	2.7	2.0	3.0	4.2	3.3	3.6	5.4
	N_2	2.0	6.8	2.9	3.3	1.5	2.9	3.3	3.4	4.6	4.3	3.3	1.9	4.3	7.7	4.7
	CO_2	0.7	0.7	0.7	0.7	0.6	0.7	1.3	0.7	0.7	0.7	0.5	0.8	1.3	2.7	2.0
Pb	Air	1.3	0.7	0.7	1.0	1.0	0.9	1.6	0.7	1.2	3.9	0.5	0.6	2.9	3.1	6.8
	N_2	1.0	1.0	0.9	1.2	2.0	1.5	0.7	1.6	6.6	4.8	1.0	0.7	3.8	3.9	7.0
	CO_2	0.7	1.3	0.7	1.3	0.7	0.7	0.7	0.7	1.3	0.7	2.0	1.3	1.3	2.7	3.1
Zn	Air	2.0	3.8	1.0	2.8	1.0	<0.1	0.7	1.4	5.7	0.7	2.4	2.4	4.2	8.9	8.4
	N_2	5.3	3.7	3.0	3.7	1.2	1.0	0.7	2.0	6.3	1.6	3.5	2.7	6.7	15.6	8.9
	CO_2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.7	<0.1	<0.1
Cd	Air	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.7	<0.1	<0.1
	N_2	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.7	<0.1	<0.1	0.7	<0.1	<0.1	<0.1
	CO_2	4.0	4.0	3.3	8.0	5.3	6.0	3.3	3.3	2.7	4.0	4.6	8.0	3.3	5.3	4.0
As	Air	8.0	7.3	15.3	14.0	11.3	14.6	14.0	7.3	12.6	5.3	14.0	12.0	16.0	12.0	13.3
	N_2	14.0	12.6	19.6	15.6	13.7	16.3	16.6	16.0	16.0	13.2	14.9	13.6	19.3	17.8	19.3
	CO_2	0.8	0.9	1.0	1.1	1.0	0.4	0.5	0.1	0.1	0.3	0.5	0.4	0.4	3.1	0.8
Hg	Air	1.7	1.5	2.8	3.0	2.8	3.7	2.2	0.8	1.0	0.8	0.9	3.0	3.1	2.4	2.3
	N_2	3.6	3.2	3.4	16.0	3.1	3.9	4.1	1.0	2.6	1.6	3.2	4.9	7.5	6.5	4.5

Table B.4: Leachate metal concentration for waste 2 specimens (mg/L)

Waste 2 or Metal Colour Waste Specimens

Metals	Environ.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	CO_2	2.7	6.6	3.3	6.0	1.3	8.0	7.3	3.4	8.6	5.3	5.3	9.3	12.6	1.3	1.3
Cr	Air	10.0	10.1	17.9	10.0	2.0	9.2	16.0	14.6	20.0	21.3	6.0	12.6	13.2	2.0	1.3
	N_2	7.3	25.3	3.3	11.0	0.7	20.0	11.3	9.3	11.3	4.6	20.0	14.9	17.7	0.7	4.0
	CO_2	<0.1	<0.1	2.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.7	0.7	<0.1	<0.1
Cu	Air	<0.1	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	N_2	0.7	0.7	10.1	<0.1	<0.1	0.7	0.7	0.7	0.7	0.7	<0.1	0.7	0.7	<0.1	<0.1
	CO_2	0.7	<0.1	2.4	20.3	3.2	1.0	0.5	2.7	1.0	3.3	1.3	12.6	10.2	39.2	81.4
Ni	Air	2.0	1.3	10.3	19.4	3.9	22.6	8.2	3.9	2.3	2.8	0.7	0.7	49.2	40.1	72.3
	N_2	4.7	2.0	15.9	32.3	2.8	29.9	12.4	5.0	4.9	24.5	0.7	19.3	87.1	40.0	80.0
	CO_2	1.3	2.0	10.2	4.1	10.9	3.0	2.0	6.3	3.9	9.3	3.3	15.9	0.7	20.0	21.1
Pb	Air	2.7	10.0	15.0	6.9	9.4	12.9	3.4	4.2	4.1	12.0	2.0	33.1	2.0	18.2	34.6
	N_2	0.7	7.9	11.0	12.3	11.3	17.1	5.2	9.0	9.8	20.2	4.0	61.2	19.5	29.3	23.4
	CO_2	1.3	9.0	3.0	7.3	<0.1	3.3	7.9	29.4	1.3	2.1	10.3	2.7	49.2	2.7	29.6
Zn	Air	15.3	8.6	16.6	24.0	6.0	8.0	6.6	8.0	12.7	4.0	39.4	7.3	9.4	1.3	20.2
	N_2	86.0	14.8	7.3	42.0	10.9	38.6	79.7	12.3	34.6	9.3	61.2	9.3	9.2	10.0	16.6
	CO_2	0.7	1.3	6.6	10.6	<0.1	2.0	<0.1	29.0	1.3	6.0	0.7	7.3	6.6	<0.1	<0.1
As	Air	6.6	5.0	3.3	6.6	2.0	4.6	3.3	8.5	4.0	4.0	4.4	6.0	5.3	3.3	0.7
	N_2	7.3	12.2	5.3	7.3	4.0	6.0	4.6	12.9	4.4	4.6	4.9	6.6	5.3	3.2	4.9

APPENDIX C

This Appendix gives the results from the Eudiometer test for all waste/binder systems studied in this work. The mixes (M), 1 to 40, are related to Figure 5.2 (Chapter 5).

Table C1: Eudiometer results - Control Samples: A = Total CO_2 uptake (%CO_2 /w/w solids); B = Rate of carbonation (%CO_2 /min.)

	opc		opc/pfa		opc/ggbs		wopc		wopc/pfa		wopc/ggbs		srpc		srpc/pfa		srpc/ggbs	
M	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	0.8±0.31	0.002	0.61±0.22	0.001	0.99±0.33	0.001	0.72±0.44	0.01	0.79±0.52	0.001	0.34±0.20	0.001	1.0±0.31	0.02	1.3±0.90	0.02	1.0±0.87	0.01
2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	1.1±0.81	0.01	0.92±0.74	0.001	1.1±0.34	0.01	0.98±0.38	0.001	0.41±0.29	0.001	0.20±0.18	0.001	0.88±0.42	0.001	0.91±0.32	0.001	0.74±0.45	0.001
4	0.9±0.24	0.003	1.0±0.87	0.002	0.62±0.49	0.001	0.42±0.22	0.001	0.22±0.12	0.001	nd	nd	0.62±0.50	0.001	0.24±0.19	0.001	0.55±0.32	0.001
5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
6	2.1±0.74	0.04	2.0±0.30	0.05	1.9±0.92	0.03	1.2±0.72	0.04	0.93±0.70	0.01	1.1±0.29	0.02	1.7±0.98	0.01	2.0±1.1	0.02	1.8±0.42	0.01
7	1.9±0.92	0.01	1.0±0.32	0.02	1.2±0.65	0.03	1.0±0.67	0.001	0.80±0.59	0.001	1.0±0.30	0.01	1.1±0.20	0.001	1.0±0.11	0.001	0.84±0.75	0.001
8	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	2.5±1.0	0.09	2.2±0.77	0.1	2.0±0.93	0.04	2.7±0.32	0.09	2.0±0.76	0.10	2.5±0.58	0.12	2.9±1.0	0.09	3.2±0.89	0.05	2.0±0.18	0.03
11	1.2±0.98	0.10	2.3±0.87	0.09	1.82±0.89	0.01	1.90±0.99	0.03	1.2±1.0	0.07	1.6±0.62	0.02	2.0±0.19	0.03	2.6±1.3	0.03	1.3±0.48	0.01
12	2.0±0.22	0.01	1.3±0.75	0.002	1.9±0.24	0.04	2.0±0.41	0.03	1.0±0.14	0.01	1.7±0.40	0.01	1.0±0.55	0.01	1.7±0.55	0.01	2.2±0.89	0.04
13	1.7±0.87	0.03	1.9±0.44	0.05	1.0±0.52	0.01	1.0±0.18	0.01	0.64±0.22	0.001	0.80±0.59	0.001	0.7±0.29	0.001	0.99±0.31	0.001	0.35±0.24	0.001
14	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
15	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
16	5.5±1.2	0.36	4.2±1.1	0.26	4.7±1.2	0.19	4.6±1.3	0.10	5.8±1.5	0.22	3.9±0.99	0.17	5.0±1.6	0.21	4.9±1.0	0.29	4.1±0.25	0.31
17	4.9±1.6	0.40	5.5±0.89	0.19	3.3±1.9	0.06	3.7±0.72	0.03	3.8±1.3	0.20	2.7±0.21	0.12	4.9±0.84	0.20	3.7±0.59	0.21	4.5±0.51	0.18
18	4.0±1.0	0.40	4.4±0.21	0.16	2.3±0.79	0.02	1.9±0.34	0.01	1.8±0.12	0.02	2.6±0.88	0.06	4.2±2.3	0.11	4.0±1.4	0.12	3.2±0.46	0.10
19	2.3±0.90	0.21	2.7±0.51	0.09	1.5±1.3	0.08	3.0±0.42	0.04	2.0±0.98	0.03	1.9±0.35	0.07	3.8±0.59	0.09	4.2±0.97	0.09	2.0±0.39	0.01
20	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
21	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
22	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
23	6.7±1.82	0.30	4.7±1.90	0.17	2.5±0.93	0.09	2.8±1.0	0.03	2.2±0.13	0.05	3.1±1.6	0.09	7.2±0.47	0.20	7.6±0.51	0.17	6.1±0.22	0.10
24	5.3±0.88	0.28	1.7±0.56	0.10	3.8±0.93	0.18	0.9±0.53	0.009	1.9±1.0	0.02	0.6±0.11	0.001	5.9±0.22	0.10	6.0±0.97	0.10	6.2±0.90	0.08
25	2.1±1.8	0.09	1.3±1.0	0.08	2.8±0.91	0.06	1.7±0.44	0.01	0.5±0.19	0.001	1.8±0.26	0.01	2.1±0.35	0.08	2.3±0.12	0.02	1.8±0.26	0.01
26	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
27	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
29	6.2±0.32	0.43	3.2±1.2	0.19	4.9±0.77	0.26	3.4±0.11	0.10	3.3±1.2	0.15	2.1±0.81	0.02	6.5±1.1	0.29	6.0±0.29	0.16	3.2±0.78	0.12
30	4.9±0.71	0.31	1.6±0.15	0.10	2.8±0.49	0.14	1.0±0.72	0.01	1.7±1.0	0.10	0.4±0.14	0.001	2.2±0.38	0.10	3.8±0.59	0.08	2.1±0.41	0.09
31	3.2±0.99	0.10	0.7±0.91	0.08	1.4±0.32	0.10	1.6±0.68	0.04	0.5±0.29	0.001	1.3±0.91	0.01	1.4±0.67	0.07	2.6±1.3	0.02	1.0±0.66	0.01
32	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
33	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
34	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
35	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
36	3.2±1.8	0.21	4.0±0.20	0.19	7.1±0.35	0.31	2.4±0.87	0.02	2.4±0.76	0.09	1.4±0.90	0.05	3.9±1.0	0.10	4.6±0.88	0.12	3.0±0.32	0.09
37	4.8±0.31	0.12	3.0±0.71	0.10	6.7±1.4	0.28	0.80±0.31	0.03	1.0±0.33	0.03	0.4±0.27	0.001	2.9±0.23	0.08	3.2±0.70	0.06	2.1±0.81	0.07
38	1.1±0.69	0.08	0.9±0.41	0.09	1.1±0.42	0.01	0.90±0.10	0.006	0.8±0.61	0.001	1.0±0.64	0.008	1.7±0.47	0.01	1.9±0.44	0.02	1.0±0.12	0.01
39	1.1±0.12	0.01	1.5±0.77	0.08	2.2±0.38	0.10	0.72±0.43	0.005	0.62±0.10	0.001	1.2±0.78	0.007	0.76±0.50	0.001	1.0±0.54	0.001	0.70±0.60	0.001
40	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table C.2: Eudiometer results - Waste 1 Samples: A = Total CO_2 uptake (% CO_2 /w/w solids); B = Rate of carbonation (% CO_2/min.)

	opc		opc/pfa		opc/ggbs		wopc		wopc/pfa		wopc/ggbs		srpc		srpc/pfa		srpc/ggbs	
M	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	2.0±0.79	0.09	1 2±0 37	0 02	1.9±0.21	0.01	1 8±0.34	0.03	2 2±0.78	0 01	2.8±0 41	0 06	2.7±0.51	0.02	2.3±0.49	0.03	2.9±0.78	0.02
2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	2.8±1.2	0.02	2.0±1.1	0.01	2 9±0.13	0 02	2 6±0.55	0.10	2 7±0.39	0 09	3.1±0 52	0.12	3 0±0.31	0.07	2.7±1.2	0.05	3 2±1.7	0.07
4	1.2±0.12	0.008	1 0±0.22	0.001	0.74±0.28	0.001	1 0±0 27	0.001	0 8±0 44	0 001	1.0±0.84	0 001	1.0±0.51	0.002	1.3±0.69	0.002	0.7±0.12	0.001
5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
6	7.2±0.78	0.20	3 3±0.37	0 02	4 3±0.25	0 09	4 2±1.9	0 12	4 7±0.39	0 10	5.9±1 6	0 14	6.9±0.91	0.17	6.1±0 32	0.10	7.2±0.11	0.12
7	16 0±0.93	0.36	5.4±1.2	0.04	11 6±0.73	0.23	3 6±0 98	0.08	2 8±1.7	0 04	4 0±0 12	0.05	7.9±0.14	0.25	7.0±1.3	0.19	8.1±0.24	0.023
8	8.8±0.16	0.29	2.9±0.78	0.02	6.1±0.59	0.10	1 3±0.87	0 002	0 72±0.10	0.001	1 0±0 63	0 001	8.7±0.41	0.27	7.9±0.14	0.25	8.9±0.32	0.32
9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	5.6±1.4	0.10	5.0±1.1	0.07	7.2±1.9	0.12	6.4±1.3	0.13	5.1±0.77	0.14	5.7±0.33	0.16	6.5±1.0	0.17	5.2±0.38	0.15	6.9±1.0	0.12
11	6.3±0.12	0.13	5.3±0.79	0.08	6.5±1.7	0.09	5.3±0 25	0.10	4 3±0 39	0.07	5.0±1.0	0.09	5.9±0.72	0.18	5.0±0.84	0.12	6.1±0.10	0.10
12	10.1±0 65	0.18	4.9±0.74	0.06	5.0±0.81	0.10	4 8±0.39	0.06	3 9±0.87	0.05	3.2±0.68	0.02	7.7±0.49	0.10	4.3±1.3	0.02	7.5±0.24	0.19
13	14.7±1.8	0.30	3.6±0.98	0 06	9 8±0.78	0.18	7 3±0 41	0.21	6 8±1 9	0 16	7 0±0 13	0.19	8.1±0.93	0 20	2 9±0.12	0.04	8.2±0.51	0.27
14	12 0±0.11	0.29	2 6±0.57	0 01	8 4±0 88	0 21	1.2±0 78	0 002	0.7±0 24	0 001	nd	nd	11 0±1.3	0 26	2.0±0.39	0 02	7.3±0.71	0 13
15	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
16	8.4±1.7	0.10	11.2±1.4	0.33	5.7±0.43	0.12	5.3±0.38	0.14	5 0±0 13	0.25	4 2±0.72	0.09	7.3±0.15	0.22	8 4±0 88	0.16	7.0±0 67	0.17
17	7.2±1.3	0.11	10 8±1.9	0.21	4 3±1 0	0 07	4 1±0.29	0.12	4 7±1.7	0 17	2 4±0.99	0 01	6.7±0 51	0.24	7.8±0.13	0.14	6.4±0.22	0.10
18	6.1±0.29	0.15	8 0±2.6	0 16	3 9±0.34	0.04	6.9±0.36	0.10	5 0±0.12	0.18	2 0±0.15	0 01	5.9±0.33	0.12	7.0±0.40	0.08	5.2±0.89	0 09
19	5.6±0.78	0.18	5 3±0.28	0.06	13 3±0.52	0.3	7.4±1.1	0.16	2.1±0.28	0.34	7 6±2.0	0.21	4 1±0.12	0.10	6 0±0.64	0.11	7.6±0 69	0.03
20	13.5±0 41	0.39	4.2±0 77	0.03	6.8±0.99	0.11	1.5±0 49	0 02	1.8±0.34	0.02	5.9±0 36	0.002	8 8±0 27	0.09	4 8±0 81	0.01	7.1±0.50	0.02
21	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
22	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
23	9.9±2.1	0.20	8.3±0.47	0.17	5.9±2.0	0.10	3.1±0.23	0.11	2.3±0.36	0.17	6 3±1.0	0.30	6 4±0.14	0.28	8.9±0.79	0.14	7.5±0.97	0.20
24	7.3±1.1	0.12	5 6±0.83	0.15	6 6±1.3	0.13	5.1±0.47	0.23	7.7±1.4	0 33	3 7±0.39	0.16	5 9±0.26	0.11	7.7±0.88	0.10	6 8±0.13	0.11
25	2 6±0.25	0.03	3.1±0.22	0.08	7.5±1.2	0.24	2 3±0.19	0.02	2.2±0.95	0.01	1.5±0.46	0.03	2 6±0.84	0.02	4.2±0 65	0.06	4 1±0.19	0.09
26	10 1±1.5	0.29	1.0±0 89	0.001	1.2±0.60	0.002	nd	nd	nd	nd	nd	nd	7.9±0.72	0.11	nd	nd	nd	nd
27	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
29	6.2±1.3	0.10	7.7±0.93	0.19	4.9±0.22	0.10	3 0±0.79	0.03	6.7±0 66	0.17	3.4±0.51	0.23	6.6±1.2	0 21	8.0±0 24	0.18	5.3±0 45	0.09
30	6 0±1.7	0.07	13.0±1.8	0.24	2 1±0.66	0.05	4.2±1.2	0.04	4 0±0.33	0.21	2.7±0.72	0.10	5.7±018	0.09	8.2±0.87	0.20	3.7±0.99	0.03
31	4.1±0.79	0.03	8 6±1.9	0.21	1.3±0.78	0.02	1.8±0.17	0.03	0.6±0.24	0.007	1.1±0.56	0.008	5.0±0.72	0.08	6.1±0.73	0.12	2.0±0.87	0.04
32	1.8±0.64	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
33	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
34	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
35	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
36	2.8±1.0	0.09	0.6±0.25	0.001	2 8±0.17	0 03	4.1±1.3	0 24	2 1±0 34	0.02	3.4±0.98	0.16	5.7±0.83	0.14	4.2±0.38	0.12	2.9±0.54	0.15
37	1.3±0.76	0.02	0.8±0.52	0.001	1.1±0.24	0.01	1 6±0.10	0.03	1.1±0.49	0.04	1.0±0.77	0.009	3.4±0.47	0.11	3.9±0.72	0.10	1.4±0.16	0.01
38	3.4±0.59	0.08	1.0±0.74	0.01	1.6±0.58	0.04	1.1±0 29	0.02	1.2±0.81	0.03	0.6±0.33	0.006	1.2±0.22	0.001	0.98±0 66	0.001	1.0±0.10	0.001
39	1.0±0.28	0.001	nd	nd	1.0±0.36	0.001	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
40	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table C.3: Eudiometer results - Waste 2 Samples: A = Total CO_2 uptake (% CO_2 /w/w solids); B = Rate of carbonation (% CO_2/min.)

	opc		opc/pfa		opc/ggbs		wpc		wpc/pfa		wpc/ggbs		srpc		srpc/pfa		srpc/ggbs	
M	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	3.2±0.16	0.09	2.5±0.33	0.07	3.0±0.92	0.08	2.1±0.12	0.01	2.0±0.39	0.01	1.8 0.46	0.004	3.9 0.89	0.08	2.9 0.45	0.02	3.3 0.56	0.03
2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	3.9±0.38	0.01	2.6±0.44	0.02	4.1±1.3	0.05	2.9±0.78	0.02	2.5±0.84	0.03	2.0 0.12	0.01	4.2 0.99	0.06	3.7 0.33	0.02	3.8 0.23	0.04
4	1.7±0.13	0.001	1.1±0.57	0.001	1.8±0.98	0.005	2.2±0.91	0.01	1.7±0.75	0.01	1.3±0.61	0.004	2.1 0.70	0.001	1.1 0.22	0.001	1.4 0.59	0.002
5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
6	4.3±0.21	0.09	3.8±0.36	0.05	5.2±0.67	0.08	3.5±0.92	0.04	3.1±0.35	0.01	3.0 0.91	0.02	4.7 1.3	0.10	3.7 1.4	0.10	4.0 0.11	0.13
7	2.2±0.84	0.002	1.9±0.18	0.001	3.0±0.48	0.009	2.7±0.84	0.02	2.0±0.71	0.01	1.8 0.87	0.09	2.4 0.15	0.01	1.5 0.91	0.008	1.8 0.47	0.002
8	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	6.4±1.3	0.09	5.9±0.92	0.10	6.0±0.33	0.10	3.9±0.45	0.02	2.7±0.72	0.03	2.4 0.21	0.02	4.9 0.19	0.10	4.0 0.42	0.07	3.8 0.66	0.04
11	8.2±0.12	0.20	4.8±0.84	0.05	4.7±0.96	0.04	3.0±0.38	0.03	2.0±0.81	0.01	1.9 0.10	0.01	5.7 0.49	0.11	4.4 0.77	0.10	6.7 0.55	0.14
12	2.4±0.71	0.25	3.2±0.82	0.04	5.1±0.96	0.12	2.1±0.71	0.01	1.6±0.67	0.001	1.2 0.41	0.007	6.6 0.11	0.32	5.0 0.80	0.15	7.1 0.13	0.11
13	5.1±0.84	0.04	2.1±0.81	0.01	2.0±0.12	0.01	1.6±0.15	0.04	1.0±0.71	0.007	0.94 0.52	0.001	5.2 0.99	0.01	3.1 0.41	0.01	4.4 0.33	0.06
14	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
15	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
16	5.2±1.4	0.07	5.0±0.79	0.03	4.9±0.21	0.08	4.0±1.2	0.12	5.1±0.21	0.03	4.4 0.31	0.01	4.6 1.0	0.05	4.0 0.22	0.02	5.1 0.34	0.02
17	4.7±0.12	0.08	3.5±0.34	0.06	3.8±0.44	0.09	4.3±0.21	0.15	4.7±1.1	0.04	3.2 0.22	0.03	3.2 0.76	0.08	3.0 0.57	0.03	2.9 0.24	0.01
18	5.1±0.88	0.03	4.2±1.1	0.05	8.4±0.28	0.17	4.9±0.42	0.10	5.0±0.29	0.05	6.8 0.71	0.09	4.1 0.14	0.10	3.3 0.94	0.05	2.1 0.32	0.02
19	7.1±1.4	0.12	2.0±0.10	0.02	10.2±0.33	0.10	5.3±0.71	0.03	5.3±0.56	0.23	8.4 0.74	0.17	4.0 0.27	0.06	6.0 0.88	0.10	6.2 0.62	0.08
20	1.7± 81	0.01	2.2±0.73	0.02	12.0±0.78	0.08	3.3±0.16	0.02	3.3±0.24	0.48	2.9±0.28	0.03	1.2±0.17	0.02	1.0±0.45	0.01	0.9±0.61	0.002
21	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
22	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
23	3.2±0.47	0.03	3.2±0.46	0.05	8.8±1.6	0.12	2.2±0.31	0.11	3.4±0.93	0.09	2.2 0.72	0.11	2.0 0.19	0.08	1.8 0.99	0.14	2.8 0.34	0.12
24	7.4±0.99	0.10	11.1±0.99	0.39	5.1±1.2	0.07	7.7±0.18	0.32	3.8±0.49	0.17	2.2 0.17	0.02	1.4 0.87	0.02	1.9 0.13	0.09	1.6 0.83	0.08
25	2.3±0.21	0.05	1.5±0.19	0.01	2.0±1.0	0.02	8.0±0.24	0.33	2.4±0.56	0.02	0.9 0.19	0.008	1.0 0.91	0.002	1.2 0.15	0.001	0.72 0.43	0.001
26	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
27	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
29	4.6±0.24	0.14	7.0±0.97	0.11	3.4±0.34	0.03	2.0±0.92	0.02	2.1±3.2	0.02	1.6 0.16	0.02	4.1 0.99	0.16	5.2 0.44	0.18	5.9 0.61	0.18
30	7.2±0.58	0.16	5.5±0.81	0.12	2.1±0.22	0.02	2.9±0.91	0.03	3.5±0.41	0.23	1.4 0.39	0.01	5.6 0.70	0.11	6.6 1.5	0.19	5.8 0.23	0.13
31	1.8±0.31	0.01	1.6±0.58	0.01	1.9±0.34	0.01	1.5±0.24	0.01	1.0±0.25	0.001	0.8 0.51	0.007	1.0 0.87	0.01	4.1 0.30	0.12	3.2 0.41	0.10
32	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
33	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
34	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
35	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
36	5.2±0.81	0.10	6.6±0.42	0.09	2.9±0.31	0.06	1.8±0.28	0.02	3.3±0.99	0.21	2.1 0.72	0.12	4.5 1.2	0.10	3.3 0.48	0.07	4.0 0.23	0.09
37	1.2±0.72	0.09	0.7±0.35	0.01	2.2±0.17	0.03	0.80±0.34	0.001	4.7±0.84	0.15	1.5 0.24	0.08	1.5 0.86	0.004	1.0 0.79	0.002	1.1 0.48	0.03
38	1.3±0.34	0.01	1.3±0.22	0.01	0.82±0.11	0.001	1.3±0.81	0.002	0.6±0.80	0.005	0.6 0.50	0.006	1.0 0.74	0.001	0.8 0.30	0.002	0.34 0.17	0.001
39	2.7±0.21	0.03	nd	nd	0.81±0.10	0.003	0.40±0.24	0.001	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
40	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

APPENDIX D

This Appendix gives details of the microprobe analysis carried out on polished samples of different carbonated mixes. In Figure D.1, an illustration of the main areas analysed by EDXA are given. Table D.1 shows the results from samples prepared with industrial waste/OPC (Chapter 6) and single metal solutions, doped-cement (Chapter 7).

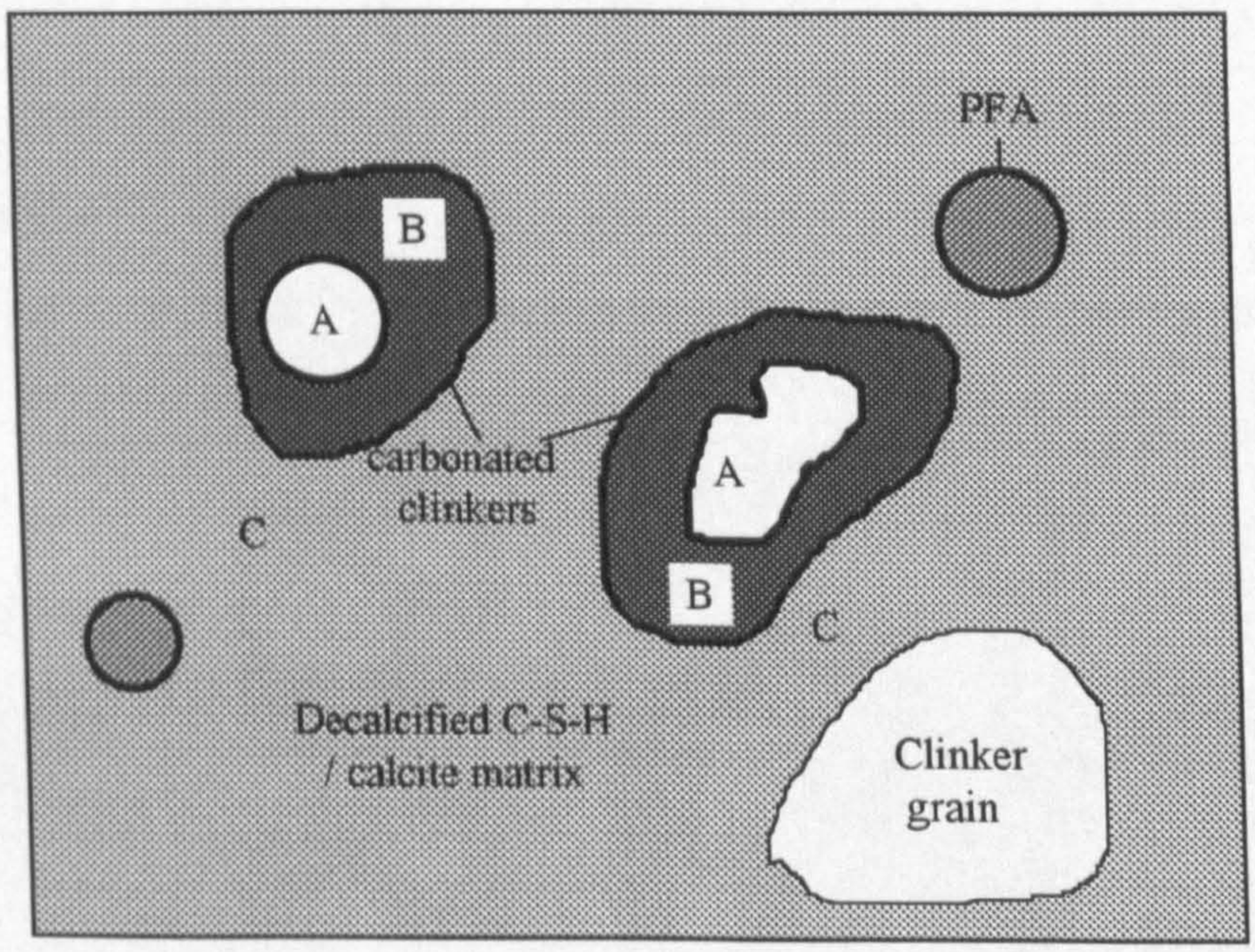


Figure D.1: Typical carbonated OPC/waste matrix, where: A = unreacted C_3S; B = Dark silica rich rim; C = Carbonated matrix

Table D.1: Microprobe analysis for selected mixes

Sample	Area Analysed	Comments	SiO2%	Al2O3%	Fe2O3%	TiO2%	Mn2O3%	MgO%	CaO%	K2O%	SO3%	Cl%	NiO%	ZnO%	Cr2O3%	PbO%	CdO%	HgO%	CuO%	P2O5%	Ca:Si
1W1A	50 mm	paste	20 03	4 02	2	0 27	0 1	0 97	60 38	0 74	4 2	1 25	0	2 01	1 05	1 21	0	0 16	1 04	0 58	3 01
1W1A	spot	clinker grain	24 02	0 72	0 75	0	0 07	0 41	72 39	0 67	0 09	0 06	0	0 18	0	0 14	0 12	0 3	0	0 69	3 01
1W1A	30 mm	gel-carbonated	30 59	5 57	2 47	0 37	0 14	1 64	50 33	0 03	4 31	0 18	0	0	4 29	0 61	0	0	0 35	0 55	1 64
1W1A	50 mm	gel-carbonated	23 54	4 14	1 47	0 38	0 09	0 32	61 8	0 54	3 06	0 09	1 54	2 32	0 51	0	1 58	0	0	0	2 63
1W1A	100 mm	gel-carbonated	23 76	5 89	3 03	0 31	0	1 62	59 98	0 69	3 09	0 12	0	1 43	0 08	0	0	0	0	0	2 52
1W1A	spot	gel-carbonated	10 27	1 13	1 92	0 05	0	0 17	77 63	0 45	2 08	0 33	0	3 88	1 02	0 58	0	0 42	0	0 58	7 5
1W1A	spot	gel infilling pore	18 46	3 08	13 02	0 47	0 4	2 55	44 74	0 37	4 7	1 11	0 45	2 73	2 84	1	0 4	0	1 77	0	0 26
1W1A	spot	reacted C3S - rim close to gel	68 61	4 24	3 87	0 93	0 17	1 58	12 04	3 63	0 55	0 11	0	3 36	0	1	0	0	0	0	0 73
1W1A	spot	reacted C3S - rim half way	49 17	1 92	0 93	0 3	0 05	2 49	10 96	1 54	1 72	1 83	0	8 73	2 14	7 2	3	0	0	0	0 4
1W1A	spot	reacted C3S - rim close to clinker	34 58	1 46	2 01	0 12	0 04	0 77	36 58	0 53	0 17	0 16	0 14	0 24	0 04	0 17	0	0	0 02	0	1 06

Sample	Area Analysed	Comments	SiO2%	Al2O3%	Fe2O3%	TiO2%	Mn2O3%	MgO%	CaO%	K2O%	SO3%	Cl%	NiO%	ZnO%	Cr2O3%	PbO%	CdO%	HgO%	CuO%	P2O5%	Ca:Si
1W2A	50 mm	paste	18 87	3 85	2 24	0 2	0 05	0 88	64 33	0 62	1 08	0 14	0 97	5 01	0 39	1 47	-	-	0 39	0 75	3 41
1W2A	spot	clinker grain	29 2	1 31	1 57	0 14	0	0 42	66 33	0 39	0 26	0 05	-	0 19	0 03	0 25	-	-	0 06	0	2 27
1W2A	50 mm	gel-carbonated	28 92	2 48	0 06	0 2	0 15	1 61	58 98	0 86	2 2	0 16	1 46	3 29	0 84	0	-	-	2 42	0	2 04
1W2A	100 mm	gel-carbonated	4 42	0 75	0 23	0 12	0 16	0 42	45 39	0 19	1 25	0 04	3 07	7 43	1 23	2 11	-	-	2 31	0	10 3
1W2A	spot	gel-carbonated	18 46	3 09	13 02	0 47	0 4	2 55	44 74	0 37	4 7	1 14	0 45	3 73	2 84	1	-	-	0 4	1 06	2 42
1W2A	spot	gel-carbonated	10 64	0 79	0 19	0 07	0	0 63	47 07	0 09	2 76	0 13	2	4 14	3 07	1 24	-	-	1 12	0	4 42
1W2A	spot	gel infilling pore	4 18	1 07	2 09	0	0 33	0 02	80 07	0 23	1 77	0 17	3 57	5 63	2 38	1 39	-	-	0 11	0	19 2
1W2A	spot	reacted C3S - rim close to gel	67 14	2 08	1 86	0	0 17	1 27	12 06	4 24	1 05	0	2 21	2 016	3 75	1 99	-	-	0	0	0 18
1W2A	spot	reacted C3S - rim half way	51 19	1 29	0 94	0 16	0 03	0 89	20 96	1 5	0 03	0 09	2 99	8 42	1 03	4 39	-	-	0	0	0 41
1W2A	spot	reacted C3S - rim close to clinker	34 13	0 89	1 22	0 22	0 02	0 82	32 49	0 12	0 88	0 15	0 87	3 31	0 04	3 42	-	-	0	0	0 95

Sample	Area Analysed	Comments	SiO2%	Al2O3%	Fe2O3%	TiO2%	Mn2O3%	MgO%	CaO%	K2O%	SO3%	Cl%	NiO%	ZnO%	Cr2O3%	PbO%	CdO%	HgO%	CuO%	P2O5%	Ca:Si
10%Zn	spot	clinker	29 32	1 77	1 3	0 36	0 02	0 46	66 47	1 24	0 63	0 01	-	0 11	-	-	-	-	-	-	2 3
10%Zn	spot	gel-carbonated	6 4	1 65	0 73	0 11	0 04	0 33	86 2	0 98	1 49	0 01	-	2 06	-	-	-	-	-	-	13 5
10%Zn	spot	gel-carbonated	1 79	0 9	0 26	0 02	0 02	0 14	50 92	0 52	1 06	0 11	-	6 11	-	-	-	-	-	-	28 4
10%Zn	spot	gel-carbonated	1 54	0 48	0 08	0 01	0 03	0 23	47 81	0 75	1 35	0 02	-	3 06	-	-	-	-	-	-	31
10%Zn	spot	reacted C3S - rim close to gel	76 55	3.57	1 95	0 75	0 17	1 07	10 16	1 21	0 63	0 05	-	1 87	-	-	-	-	-	-	0 13
10%Zn	spot	reacted C3S - rim half way	51 84	6 59	4 07	0 85	0 07	2 87	23 28	3 49	0 52	0 05	-	5 38	-	-	-	-	-	-	0 45
10%Zn	spot	reacted C3S - rim close to clinker	25 42	1 7	1 24	0 31	0 12	0 8	25 03	1 07	0 62	0 02	-	2 2	-	-	-	-	-	-	1

Sample	Area Analysed	Comments	SiO2%	Al2O3%	Fe2O3%	TiO2%	Mn2O3%	MgO%	CaO%	K2O%	SO3%	Cl%	NiO%	ZnO%	Cr2O3%	PbO%	CdO%	HgO%	CuO%	P2O5%	Ca:Si
10%Cd	spot	clinker	23 12	0 75	1.27	0 15	0 11	0 31	72 41	0 15	0 65	0 01	-	-	-	-	0 05	-	-	-	3 2
10%Cd	spot	gel-carbonated	1.13	0 98	0 15	0	0 02	0.43	54 05	0 49	0 77	0 01	-	-	-	-	6.32	-	-	-	47 8
10%Cd	spot	gel-carbonated	6.29	2 08	0.52	0.05	0	0 78	44 93	0 92	1 54	0 04	-	-	-	-	4 02	-	-	-	7.1
10%Cd	spot	gel-carbonated	2 23	1 51	2.08	0.32	0 09	0 21	51 03	0 78	1 97	0 01	-	-	-	-	7.22	-	-	-	22 9
10%Cd	spot	reacted C3S - rim close to gel	56 73	5 43	3 14	0 82	0 03	0 7	7.21	3 52	0 3	0 01	-	-	-	-	1 04	-	-	-	0 13
10%Cd	spot	reacted C3S - rim half way	27 21	3 95	3 08	0 59	0 04	0 64	15 95	2 83	1 09	0 01	-	-	-	-	2 99	-	-	-	0 59
10%Cd	spot	reacted C3S - rim close to clinker	25 42	1 7	1 24	0 31	0 12	0 8	25 03	1 07	0 62	0 02	-	-	-	-	2 28	-	-	-	0 98

Sample	Area Analysed	Comments	SiO2%	Al2O3%	Fe2O3%	TiO2%	Mn2O3%	MgO%	CaO%	K2O%	SO3%	Cl%	NiO%	ZnO%	Cr2O3%	PbO%	CdO%	HgO%	CuO%	P2O5%	Ca:Si
10%Pb	spot	clinker	29 45	3 68	1 36	0 02	0 22	2 68	59 92	0 89	0 47	0 04	-	-	-	1 32	-	-	-	-	2
10%Pb	spot	gel-carbonated	13 31	2 77	1 02	0 16	0 05	0 41	40 69	0 56	2 28	0 08	-	-	-	3 41	-	-	-	-	3 1
10%Pb	spot	gel-carbonated	15 6	3.48	1.9	0 22	0 16	0.75	60 33	0 55	2 52	0 14	-	-	-	4 83	-	-	-	-	3 9
10%Pb	spot	gel-carbonated	9 15	3	0 99	0 16	0	0 53	55 88	0 64	2 14	0 14	-	-	-	3 99	-	-	-	-	6 1
10%Pb	spot	reacted C3S - rim close to gel	68 3	0 46	0 02	0 01	0	0	11 07	0 79	0 23	0 11	-	-	-	2.38	-	-	-	-	0 16
10%Pb	spot	reacted C3S - rim half way	41 64	12 34	1 06	0 23	0	2 36	16 32	1 37	0 85	0 59	-	-	-	5.17	-	-	-	-	0 37
10%Pb	spot	reacted C3S - rim close to clinker	38 74	2 66	0 45	0 08	0 13	0	27 18	0 99	0 31	0 12	-	-	-	2 01	-	-	-	-	0 7

Sample	Area Analysed	Comments	SiO2%	Al2O3%	Fe2O3%	TiO2%	Mn2O3%	MgO%	CaO%	K2O%	SO3%	Cl%	NiO%	ZnO%	Cr2O3%	PbO%	CdO%	HgO%	CuO%	P2O5%	Ca:Si
10%Ni	spot	clinker	20 24	3 48	1.36	0.17	0 02	0 92	32 9	0 75	1 25	0 19	0 9	-	-	-	-	-	-	-	1 6
10%Ni	spot	gel-carbonated	10 12	5 2	2 25	0 23	0 01	0 95	60 3	0 15	1.48	0 16	3.72	-	-	-	-	-	-	-	5 9
10%Ni	spot	gel-carbonated	6 35	4 34	2 19	0.14	0 03	1 66	79.71	0 39	0 98	0 11	5 84	-	-	-	-	-	-	-	12 5
10%Ni	spot	gel-carbonated	8 73	2.31	1 04	0 12	0 04	0 12	77 49	0 77	1.22	0 03	6 75	-	-	-	-	-	-	-	8 9
10%Ni	spot	reacted C3S - rim close to gel	67.3	0	0 09	0	0 04	0	6 2	1 16	0 05	0 01	2 2	-	-	-	-	-	-	-	0 1
10%Ni	spot	reacted C3S - rim half way	44 58	1 37	1 27	0	0 03	0 51	12 4	1 92	0	0	3 09	-	-	-	-	-	-	-	0 28
10%Ni	spot	reacted C3S - rim close to clinker	29 35	1 92	0 65	0 13	0 04	0 17	28 95	1 91	0 39	0 01	1 24	-	-	-	-	-	-	-	1

LIST OF PUBLICATIONS WHICH HAVE RESULTED FROM THIS WORK

Publications in Journals:

Lange, L.C.; Hills, C.D. and Poole, A.B. Preliminary Investigation into the Effects of Carbonation on Cement Solidified Hazardous Waste. *Environmental Science & Technology*. **30:** 25 (1996).

Lange, L.C.; Hills, C.D. and Poole, A.B. Effect of Carbonation on Properties of Blended and Non-Blended Cement Solidified Waste Forms. *Journal of Hazardous Materials* (in press).

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Lange, L.C.; Hills, C.D. and Poole, A.B. Investigation of Carbonated Mixed Metals Solidified Waste. *Cement and Concrete Science Conference*. Oxford, UK, September, 1994.

Lange, L.C.; Hills, C.D. and Poole, A.B. Factors Affecting the Rate of Carbonation of Solidified Hazardous Waste. *Proc. Int. Conf. of Waste Stabilisation and Solidification.* Nancy, France, 28 November - 01 December, 1995.

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